# FIFTEENTH COLLOQUIUM
ON HIGH RESOLUTION
MOLECULAR SPECTROSCOPY

Strathclyde University,

GLASGOW

7 - 11 September 1997

Programme and Abstracts

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13. ABSTRACT (Maximum 200 words)

The Final Proceedings for Fifteenth Colloquium on High Resolution Molecular Spectroscopy, 16 September 1997 - 20 September 1997

The Topics covered include: high-resolution molecular spectroscopy, including new experimental techniques, measurements, new analytic techniques and results, molecular databases.

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FIFTEENTH COLLOQUIUM
ON HIGH RESOLUTION
MOLECULAR SPECTROSCOPY

Strathclyde   University,
GLASGOW
7 - 11   September 1997

Programme

GLASGOW 1997

FIFTEENTH COLLOQUIUM ON HIGH RESOLUTION MOLECULAR SPECTROSCOPY

THE UNIVERSITY OF STRATHCLYDE IN GLASGOW

Local Organising Committee

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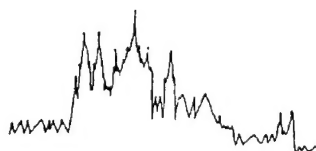
PRAHA98

The 15th International Conference on High Resolution Molecular Spectroscopy will take place in Prague, Czech Republic, August 30–September 3, 1998.

The subjects covered at this meeting are largely identical to those covered at the Fifteenth Colloquium on High Resolution Molecular Spectroscopy.

Information is available from the chairman of the local organizing committee,

Dr. Vladimír Špirko
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Dolejškova 3, CZ-18223 Praha 8, Czech Republic.
Fax: +420 2 858 2307
E-mail: praha98@jh-inst.cas.cz

The conference has a home page on the World Wide Web with URL

http://www.chem.uni-wuppertal.de/conference/

This page will be used to provide up-to-date information.

Colloquium Programme

Dates	6/9/1997	7/9/1997	8/9/1997	9/9/1997	10/9/1997	11/9/1997
Times	Saturday	Sunday	Monday	Tuesday	Wednesday	Thursday
09-00		A (9-15) Invited Lectures	E Invited Lectures	J Invited Lectures	L Invited Lectures	P Invited Lectures
10-30 to 12-30		B (10-45) Poster Session	F Poster Session	K Poster Session	M Poster Session	Q Poster Session
12-30 to 14-00		Lunch (12-45)	Lunch	Lunch	Lunch	Lunch
14-00		C (14-15) Invited Lectures	G Invited Lectures	Highland Excursion	Free Afternoon	R Invited Lectures
16-00 to 18-00	Registration starts 16-00	D(16-15) Poster Session	H Poster Session			
18-00	Buffet Supper starts 18-00	(17-30) Reception				
19-00	Registration ends 20-00	Dinner (19-30)	Civic Reception City Chambers	Banquet	Dinner	
20-00 to 22-00	Buffet ends 22-00				N Poster Session	

Programme of Sessions

FIFTEENTH COLLOQUIUM
ON HIGH RESOLUTION
MOLECULAR SPECTROSCOPY

Strathclyde   University,
GLASGOW
7 - 11   September 1997

PROGRAMME   2

SUNDAY SEPTEMBER 7   9-15

INVITED LECTURES
A
Chairman: M. Quack

A 1   Time-Resolved IR Emission Spectroscopy of Highly Vibrationally Excited
       Molecules.
       HAI-LUNG DAI.

A 2   Correlated Electronic Wave Functions for Calculations of Potential Energy Surfaces
       with High Precision.
       W. KLOPPER.

SUNDAY SEPTEMBER 7   10-45 to 12-45

POSTER SESSION
B

B 1   Improvement on Signal to Noise Ratio and Zero Transmittance Level in FTS
       records.
       L REGALIA , X. THOMAS and A. BARBE.

B 2   The REMPI and ZEKE Spectroscopy of Some Iodine van der Waals Complexes.
       D.A. BEATTTIE,, M.C.R. COCKETT, K.P. LAWLEY,R.J. DONOVAN and
       N. MCLEOD.

B 3   Analysis of of the Internal Rotation in Ethyl Nitrite with the Help of Molecular
       Beam Fourier Transform Microwave Spectroscopy.
       N. HANSEN, H. MÄDER and F. TEMPS.

B 4   Coaxially Oriented Beam-Resonator Arrangement Fourier Transform Microwave
       (COBRA-FTMW) Spectroscopy : a Cryogenic Apparatus.
       JENS-UWE GRABOW and SAMUEL PALMER.

B 5   A Supersonic Jet Experiment for IR-Spectroscopy of Small Carbon Clusters.
       U. BERNDT, T.F. GIESEN, and. G. WINNEWISSER.

B 6   Line positions and Air Broadening of Pure Rotational Transitions of BrO from FTS
       Measurements.
       G. WAGNER and M. BIRK.

B 7   Line Intensities and Self, N_2-, O_2-, and Air- Broadenings for the 3-0 band of
       $^{12}C^{16}O$.
       N. PICQUE, G. GUELACHVILI, C. CORSI. and M. INGUSCIO

2

B 8   Observation of the $\tilde{A}\,^1B_2 - \tilde{X}\,^1A_1$ Transition of SiC_2 in Carbon Stars.
      M.E HURST, T. LLOYD EVANS, and P.J. SARRE.

B 9   Integrated Absorption Coefficients for Difluoromethane in the 200 - 700 cm^{-1} Region.
      The Influence of Sample Emission.
      JON ARE BEUKES and FLEMMING M. NICOLAISON.

B 10 Photofragmentation of OCIO $\tilde{A}\,^2A_2(v_1, v_2, v_3) \rightarrow C\ell(^2P_i) + O_2$).
      R. F. DELMDAHL, S. ULLRICH and K.-H. GERICKE.

B 11 Pressure Induced Line Frequency Shifts in the v_2 Band of NH_3.
      M. IBRAHAMI, B. LEMOINE and F. ROHART.

B 12 Self and foreign gas pressure broadening and shift of the $^aQ(9,9)$ transition line of
      ammonia versus temperature.
      G. BALDACCHINI, F. D'AMATO, M. DE ROSA, and
      F. PELAGALLI, G. BUFFA and O. TARRINI.

B 13 The rotational spectrum of sodium trimer.
      L.H. COUDERT.

B 14 Accurate Calculation of the Rotatlon-Vibration Energies of HeH_2^+ Using Rayleigh-
      Schrödinger perturbation theory.
      V. SPIRKO and M. JUREK. W.P. KRAEMER.

B 15 Symmetrised Local States and Effective Dipole Moment Within a Rovibrational
      Cartesian Picture.
      V. BOUJUT, F. MICHELOT and C. LEROY.

B 16 A DVR Study of the $\tilde{A}\,^2B_1 \leftarrow \tilde{X}\,^2A_1$ Absorption Spectrum of Nitrogen Dioxide.
      D. BELMILOUD and M JACON.

B 17 High Resolution Near Infrared Electronic Spectroscopy of HCBr and DCBr.
      A.J. MARR, S. W. NORTH and T.J. SEARS, L M. RUSLEN and R W FIELD

B 18 Rydberg-Valence Interactions in the Near-Threshold Region of CO.
      P.C. HINNEN, E. REINHOLD, W. UBACHS, M. EIDELSBERG, F. LAUNAY,
      K. ITO, T. MATSUI and K-P HUBER.

B 19 Competition Between Orbital Angular Momentum and Vibrational Resonance
      Effects in the spectrum of NH_2.
      ALEXANDER ALIJAH and GEOFFREY DUXBURY.

B 20 The Pure Rotational Spectrum of ^{84}KrH AND ^{86}KrH.
      HAROLD LINNARTZ , L.R ZINK and K.M. EVENSON.

B 21 Previously Unobserved Spin Orbit Components of the e $^6\Pi$ and a $^6\Delta$ Electronic
      States of FeH.
      DANIEL.F.HULLAH, CATHERINE WILSON and JOHN M.BROWN.

B 22 Structure of aniline X (X=Ar, ^{20}Ne, ^{22}Ne)) from high resolution microwave spectroscopy.
DANIELLA CONSALVO, VOLKER STORM and
HELMUT DREIZLER

B 23 Rotational Spectrum of Coriolis Coupled Vibrational States ν_7 and ν_9 of HCOOH.
O. BASKAKOV, S. DYUBKO, and S SYROTA.

B 24 The Lowest-Frequency Parallel Fundamental Band $(\nu_s = 1 \leftarrow 0)$ of CH_3SiH_3.
J. SCHRODERUS, N. MOAZZEN-AHMADI and I. OZIER.

B 25 Ar:CO: IR-Spectroscopy and Test of Semi-empirical Potential Energy Surfaces
S. KÖNIG, S. RICHTER, I. SCHEELE and M. HAVENITH

B 26 Intensities of Interacting Bands ν_2/ν_s Fundamentals of CH_3F.
MURIEL LEPÉRE, GHISLAIN BLANQUET,
JACQUES WALRAND and GINETTE TARRAGO.

B 27 High Resolution Photoacoustic Spectrum of AsH_3 (600 A_1/E) Bands.
JIA.XIANG HAN , OLEG N. ULENIKOV , SERGI YURCHINKO, LU-YUAN
HAO; XIAO-GANG WANG, and QING-SHI ZHU.

B 28 The Analysis of the FTIR Spectrum of trans-CHCl=CHF at 800 cm^{-1}.
A. GAMBI, P. STOPPA, S. GIORGIANNI, and
M. WINNEWISSER.

B 29 The ICLAS spectrum of $^{12}C_2H_2$ between 14300 and 17500 cm^{-1}.
LUDOVIC BIENNIER, GEORG HEIMEL and
ALAIN CAMPARGUE

B 30 The Coriolis Resonating Dyad ν_4 and ν_9 of $CH_2F^{37}Cl$.
P. STOPPA, A. BALDACCI and P VISINONI.

B 31 Infrared Spectrum of $^{13}CH_3I$ in the region of the fundamental bands ν_1 and ν_4.
SEPPO ALANKO.

B 32 High resolution infrared, microwave and millimeter wave spectra, and molecular structure of $SeCF_2$.
H. BÜRGER, and W. JERZEMBECK. J. DEMAISON, P. DRÉAN, W. STAHL
and I. MERKE.

B 33 Structural and conformational properties of 1, 3- difluoropropane as studied by microwave spectroscopy and quantum chemical computations.
K-M. MARSTOKK and HARALD MØLLENDAL.

B 34 High Infrared study of the Coriolis Interacting Tetrad ν_5, ν_3, ν_6, ν_2 in FNO_2.
F. HEGELUND, H. BÜRGER and G. PAWELKE.

B 35 High resolution Laser Photoacoustic and FTIR Spectra of HCCI.
JUHA LUMMILA, OLAVI VAITTINEN, PETER JUNGNER and LAURI
HALONEN. ANNE-MARIE TOLONEN.

B.36 A combined fit to high-resolution infrared and microwave spectroscopic data for
vibrationally excited states of the ketene (CH_2CO) molecule.
L. NEMES, A. GUARNIERI and A. HUCKAUF.

B 37 Overtone spectroscopy of Ethylene.
M. BACH, R. GEORGES and M. HERMAN.

B38 Analysis of Nuclear Quadrupole Structure in FTMW Spectra of $^{14}N_2\cdots H^{35}Cl$ and
$^{14}N_2\cdots H^{37}Cl$
Z.KISIEL and L.PSZCZÓLKOWSKI, P.W. FOWLER and A.C. LEGON

B39 Application of a Modular Difference Frequency Spectrometer with Two Diode Lasers
As Pump Sources for Trace Gas Detection at Sub-ppm -level.
B. SUMPF, T. KELZ, A. SCHUMACHER and H-D. KRONFELDT

B40 Doppler-free Two-Photon Absorption Spectroscopy of the $A^1A_u \leftarrow X^1A_g$ Transition of
Trans-glyoxal
M.BABA, K. KATO, T. OONISHI and S. KASAHARA

SUNDAY SEPTEMBER 7   14-15

INVITED LECTURES
C
Chairman: M. Kregelewski

C 1   Spectroscopy of Interstellar Molecules In the Laboratory and in Space.
K. KAWAGUCHI.

C 2   Millimetre Wave Spectroscopy of Molecular Ions.
L.DORE.

SUNDAY SEPTEMBER 7   16-00

POSTER SESSION (A.M. AMAT-MILLS PRIZE NOMINATIONS)
D

D 1   Laser Velocity Modulation Spectroscopy of TiCl$^+$: Observation of the $A^3\Delta(3d^2)$
State and Deperturbation of the $X^3\Phi$-$A^3\Delta$ Complex.
C.FOCSA, J-L. FEMENIAS, T.R. HUET and B. PINCHEMEL **AM.**

D 2   Contribution to the Analysis of the $^3A_2 \leftarrow X^1A_1$ Wulf transition of ozone by high
resolution Fourier Transform Spectrometry.
D.INARD, A.J BOUVIER, R. BACIS and S. CHURASSY **AM.**

D 3   Infrared diode laser spectroscopy of the $A^2\Pi_u \leftarrow X^2\Sigma_g^+$ system of the Si_2^- anion.
ZHUAN LIU and PAUL.B.DAVIES **AM.**

D 4   Transient Line Narrowing.
W.VON KLITZING and R.J.BUTCHER **AM.**

D 5   The Rotational Spectrum of the AsH$_2$ Radical in its $\tilde{X}\,^2B_1$ state Studied by Far-
Infrared Laser Magnetic Resonance.
R.A. HUGHES, J-M. BROWN and K.M. EVENSON. **AM.**

D 6   A new Molecular beam Fourier Transform Microwave Spectrometer for the
Investigations of Transient Molecules.
N. HANSEN, H. MÄDER and F. TEMPS.

D 7   Diode-Pumped Terahertz Photomixing Spectrometer.
J.M.M.VAN ROOIJ, W.L.MEERTS. A.S. PINE and R.D. SUENRAM

D 8   An Absorption Modulation Technique in a Supersonic Jet Using Optical Scanning
System Analysis of The v_5 Band of CHCℓ_3 .
G. GAMBIEZ, F. RAYNAUD and B. LEMOINE.

D 9   Maximum Entropy Processing of Fourier Transform Spectra: Applications to
      Atmospheric Remote Sensing.
      C LEE, A.J. PHILLIPS, P.A.R. ADE, P.A. HAMILTON and I.G. NOLT.

D 10 The visible absorption spectrum of SiH_2 : Density determination in DC discharge
      and spectroscopy.
      ALAIN CAMPARGUE, DANIELE ROMANINI, NADER SADEGHI, and
      LUDVIC BIENNIER.

D 11 Calculating H_2O states up to dissaciation states using PDVR3D.
      HAMSE.Y. MUSSA and JONATHAN TENNYSON.

D 12 High temperature rotational transitions of water in sunspot and labratory spectra.
      O.L. POLYANSKY, N.F. ZOBOV, S. VITI and J. TENNYSON.

D 13 Column density measurements and profile retrieval of stratospheric trace species
      using an airborne FTIR.
      S.E. HOBBS and R.C. KIFT.

D 14 A secondary frequency standard from 776 nm to 815 nm with the iodine molecule.
      B. BODERMANN, M. KLUG, H. KNÖCKEL and E. TIEMANN.

D 15 Photodissociation of $CHBr_3$ at 193 nm and 248 nm: Observation of the
      electronically excited CH(B $^2\Sigma$, A $^2\Delta$) fragment.
      K. ERMISCH, R. WILHELM and J. LINDNER.

D 16 High resolution inverse raman spectroscopy of supersonic expansions of N_2, CH_4 and
      mixtures with He and Ar.
      J. SANTOS, I. TANARRO, D. BERMEJO and V.J. HERRERO.

D 17 Pure rotational Raman lines So(J=0.4) of H_2 : Frequencies, broadening and shifting
      coefficients as a function of temperature for different perturbers.
      X. MICHAUT, R. SAINT-LOUP, H. BERGER. M.L. DUBERNET-TUCKEY, P.
      JOUBERT, I. BONAMY and D. ROBERT.

D 18 The potential energy surface and vibrational-rotational energy levels of Hydrogen
      Peroxide.
      JACEK. KOPUT, STUART CARTER, NICHOLAS C. HANDY.

D 19 Conception of multispectrum nonlinear least squares fitting program : Application to
      CH_4
      A. HAMDOUNI, C. BOUSSIN, and A. BARBE.

D 20 Hydrogen Cyanide: Theory and Experiment.
      P. BOTSCHWINA, M. MATUSCHEWSKI, E. SCHICK, M. HORN and P.
      SEBALD

D 21 Molecular beam studies of ScNH and ScS.
      A.J. MARR, J. XIN and T.C. STEIMLE.

D 22   Rotational Analysis of Tantalum Oxide, TaO.
       A.AL-KHALILI, G. EDVINSSON, U HÄLLSTEN, A. TAKLIF, S. WALLIN and
       O LAUNILA.

D23   Microwave spectrum and structural parameters of methyl-cyclopentadienyl-
       manganese-tricarbonyl.
       O. INDRIS and W. STAHL.

D 24   Internal Rotation in the Microwave Spectrum of CH_3BCl_2 : An Improved Analysis.
       A. PETER COX and GEORGE OLE SØRENSEN.

D 25   Millimeter Wave Spectrum of Acetic Acid CH_3OOH.
       O.I BASKAKOV. , S.F. DYUBKO and S.V PODNOS..

D 26   Laser Photofragment Spectroscopy of GeH^+
       T. GIBBON, A. W. GEERS, Y. CHEN and P.J. SARRE

D27   Vibronic States of Nonrigid Molecules as an Object of a High Resolution Spectrum
       Theory
       A.TSAUNE, M.DYACHENKO AND V.GLUSHKOV.

D28   Submillimetre-Wave Kinetic Spectroscopy of CH_3O Produced by Excimer Laser
       Photolyis
       M. BOGEY, H. BOLVIN, B. DELCROIX, C. DEMUYNCK, M. HASSOUNA,
       and A. WALTERS.

D29   Microwave Spectrum and Internal Motion of the Furan-CO Van der Waals Complex
       Th. BRUPBACHER, J. MAKEREWICZ AND A.BAUDER

D30   The Calculation of the Bound and Quasibound Vibrational States for Ozone in its
       $^1B_2$ Electronic State
       O. BLUDSKY and P. JENSEN

D31   The Electric Dipole Moment of Ytterbium Monoxide
       C. LINTON, T.C. STEIMLE and D.M. GOODRIDGE,

MONDAY SEPTEMBER 8   9-10

INVITED LECTURES
E
Chairman: G. Duxbury

E 1   MOLECULAR PHYSICS LECTURE.
Rydberg States of Rare Gas Hydrides.
JAMES K.G. WATSON.

E 2   High Sensitivity Laser Spectroscopy of Molecules and Ions in the Near Infrared
Region.
THERESE R. HUET.

MONDAY SEPTEMBER 8   10-30 to 12-30

POSTER SESSION
F

F 1   Rempi Spectroscopy of 2-Methylpropanal.
N. SHAND, C. NING and J. PFAB.

F 2   Free jet absorption millimeter wave spectroscopy of saturated 7-membered rings:
1,3-Dioxepane.
A. DELL'ERBA, S. MELANDRI, W. CAMINATI and
P.G. FAVERO.

F 3   High-resolution absorption spectroscopy of ozone and its Isotopomers in the near-
infrared.
G. HILPERT, J. GUENTHER, M. BUCHNER and
K. MAUERSBERGER.

F 4 N_2-, O_2-, and Air-broadening Coefficients of the J=3$\leftarrow$2 line of CO and the
J=$34_{2,32}\leftarrow34_{1,33}$ line of O_3, Measured with Two Techniques Tunable Microwave
source and Fourier-Transform Spectroscopy.
M. BIRK, J.-M. COLMONT, D. PRIEM, G. WAGNER and
G. WLODARCZAK.

F 5   A study of the halogen oxides by infrared and far-infrared laser magnetic resonance.
F. TAMASSIA, J.M. BROWN and K.M. EVENSON.

F 6   Direct ℓ-type resonance and rotational spectra of PF_3 in the vibrational state $v_4 = 1$.
E. THIESSEN, U. WÖTZEL, H. HARDER and H. MÄDER.

F 7   Line-broadening studies of direct ℓ-type resonance transitions of PF_3 in the
vibrational state $v_4=1$.
E. THIESSEN, H. HARDER and H. MÄDER.

F 8   New high resolution analysis of the ν_3, ν_4 and ν_6 bands of D_2CO measured by
      Fourier Transform Srectroscopy.
      A. PERRIN, J.-M. FLAUD. A. PRE DOI-CROSS, M. WINNEWISSER, B.P.
      WINNEWISSER, G. Ch. MELLAU and M LOCK

F 9   Emission Spectrum of HCN at 1400 K in the Region of the Bending Fundamental.
      G.Ch. MELLAU, M. WINNEWISSER and A. MAKI.

F 10 Strong and Isotope selective effects of the $\Delta K=\pm 3$ interaction in the ground state
      and in the ν_5 infrared bands of four isotopomers of $FC\ell O_3$.
      F. MEGUELLATI, G. GRANER, K. BURCZYK, H. BÜRGER,
      G. PAWELKE and P. PRACNA.

F 11 Can Isotopic substitution change a bright state into a dark state? The case of the
      $\nu_3=1$ state of $FC\ell O_3$.
      F. MEGUELLATI, G. GRANER, K. BURCZYK and H. BÜRGER.

F 12 High resolution spectroscopy of the ν_3 band of WF_6 in a supersonic jet.
      VINCENT BOUDON, YABAI HE, ULRICH SCHMITT and MARTIN QUACK.

F 13 Ozone: Analysis of $\nu_1+2\nu_2+3\nu_3$ and $4\nu_1+\nu_3$ bands line positions and intensities.
      A. BARBE, V. G. TYUTEREV and J.J. PLATEAUX.

F 14 Information System for Modeling High Resolution Spectra of Polyatomic
      Molecules.
      A.NIKITIN, J.P. CHAMPION, V.G. TYUTEREV.

F 15 The potential energy surface and vibrational-rotational energy levels of $HOC\ell$.
      JACEK KOPUT, and KIRK A.PETERSON.

F 16 The application of a VUV-FT spectrometer and synchrotron radiation source to
      measurements of the O_2 and NO bands
      K. YOSHINO, J.R. ESMOND, W.H. PARKINSON, A.P. THORNE, J.E.
      MURRAY, G. COX, R.C.N. LEARNER, K. ITO, T. MATSUI, T. IMAJO, A.S.-
      C. CHEUNG and K.W.-S. LEUNG

F 17 A theoretical investigation of the Isocyanides H_3CCCNC, NC_3NC and HC_4NC.
      P. BOTSCHWINA, A. HEYL and M. HORN.

F 18 Calculation of Franck-Condon factors, intensities and level lifetimes for
      predissociating states in the B $\left({}^2\Sigma^-\right) - X\left({}^2\Pi\right)$ electronic transition of the
      methylidyne (CH) radical.
      L. NEMES and P. G. SZALAY

F 19 Stretch-bender calculations of the effects of orbital angular momentum and vibrational
      resonances in the spectrum of singlet methylene.
      GEOFFREY DUXBURY, BARRY D. MCDONALD and ALEXANDER ALIJAH.

F 20 The effects of vibrational resonances on Renner-Teller Coupling in triatomic
      molecules: The Stretch-Bender approach.
      GEOFFREY DUXBURY, BARRY D. MCDONALD and ALEXANDER ALIJAH,
      Ch. JUNGEN and H. PALIVAN

F 21 Perturbation and Predissociation in the $C^1\Pi_u$ State of Cs_2.
      M. BABA, S. KASAHARA and H. KATÔ.

F 22 Rotational spectra of the Cyclobutanone···HCl and Cyclobutanone···HF complexes.
      SONIA ANTOLINEZ, JUAN C. LÓPEZ, and J. L. ALONSO.

F 23 The Structure of Carbodimide.
      W.JABS, J. KOPUT , M. WINNEWISSER. S.P. BELOV, Th. KLAUS and G.
      WINNEWISSER.

F 24 Spatial Mapping of Collisionally Cooled Gas Molecules in a Cold Cell.
      CHRISTOPHER D BALL, FRANK C. DE LUCIA, YILMA ABEBE and
      ARLEN.W. MANTZ.

F 25 Intracavity Laser Spectroscopy of CO_2 Transitions from Excited States.
      V. SERDYUKOV, L. SINITSA, YU. POPLAVSKII,
      A. SHERBAKOV, M. ROMAEV, V. ORLOVSKII,
      V. TARASENKO.

F 26 An Electron Impact Slit Jet Ionization source for high Resolution Spectroscopy on
      Radicals, Ions and Ionic Complexes.
      THOMAS RUCHTI, THOMAS SPECK, E.J. BIESKE,
      HAROLD LINNARTZ and JOHN P. MAIER.

F 27 Rotationally Resolved UV-Spectroscopy of Polyatomic Molecules: DFWM of
      Benzene and REMPI of Hydrogen-Bonded Clusters.
      R.M. HELM and H.J. NEUSSER.

F 28 Quantum beat spectroscopy of jet-cooled radicals: further results.
      R.T. CARTER, H. BITTO and J.R. HUBER.

F 29 K-Window Spectrum of Water in Sunspots.
      O.L. POLYANSKY, N.F. ZOBOV, S. VITI and J. TENNYSON.
      P.F. BERNATH and L. WALLACE.

F 30 Precise Labratory Observation of the $^3P_2 \leftarrow {}^1P_1$ Transitions of ^{12}C and ^{13}C.
      H. KLEIN, F.LEWEN, R. SCHEIDER, J. STUTZKI and
      G. WINNEWISSER.

F 31 Labratory study of Monodeuterated Methane seen in the Planetary Widow near 6425
      cm^{-1}.
      C. BOUSSIN, B.L. LUTZ, C. DE BERGH and A. HAMDOUNI.

F 32 Time resolved rapid scan FT-UV spectroscopy and its application to flash
      photolysis of Br_2 and O_3.
      O. FLEISCHMANN, J. ORPHAL and J.P. BURROWS.

F 33 Fermi Resonance $v_3=1/v_5=2$ in Deuterated Iodoacetylene.
      H. SARKKINEN, A.-M. TOLONEN and S. ALANKO.

F 34 High resolution FTIR study of SiD_3F. The ground and the v_3 and $v_6=1$ and 2
      states.
      N. BEN SARI-ZIZI, and H. NAJIB.
      H. BÜRGER and E.B. MKADMI.

F 35 Determination of the NaKr X $^2\Sigma$ and the Kar B $^2\Sigma$ Interatomic potential from Laser
      spectroscopic data.
      M. BRAUNE, D. SCHWARZHANS and D. ZIMMERMANN.

F 36 Calculations of Far-wing line shapes and application to atmospheric absorption
      spectra.
      R.H. TIPPING and Q. MA.

F 37 Sub-Doppler Analysis in Collision Induced Transitions
      A. DI LIETO, S. CAROCCI, A. DE FANIS, P. MINGUZZI AND M. TONELLI.

F38   Fourier Transform Spectrum of ^{18}O AND ^{17}O Enriched OCS from 1800 to 4400
      cm^{-1}.
      T. STRUGARIUA, S. NAIM, A. FAYT, H. BREDOHL AND I. DUBOIS

F39   Effect of Spin-orbit Interaction on Energetic and Radiative Properties of the d $^1\Pi$,
      d$^3\Pi$ Complex of NaK
      A.V.STOLYAROV , E.A.PAZYUK , P.KOWALCZYK AND R.S.FERBER

F40   An Alternative Light Source for the 7 µm Region Applying Difference Frequency
      Generation in AgGaSe2
      B. SUMPF, S. UCMAZ, D. REHLE and H-D. KRONFELD

MONDAY SEPTEMBER 8   14-00

INVITED LECTURES
G
Chairman: J.M. Brown

G 1   Cavity Ring Down Spectroscopy.
      GERARD MEIJER.

G 2   Hydrogen Fluoride Cluster Dynamics via High Resolution IR Spectroscopy:
      Achievements, Limitations and Alternatives.
      MARTIN A. SUHM.

MONDAY SEPTEMBER 8   16-00

POSTER SESSION
H

H 1   First Microwave Transitions of a negative ion SH⁻ and SD⁻.
      S. CIVIS, S. BAILLEUX, M. BOGEY, A. WALTERS and M. YU.
      TRETYAKOV.

H 2   The Importance of the Higher Interrelations of the Dunham Coefficients.
      M. RYTEL.

H 3   High Resolution Mid-Infrared Molecular Absorption Spectroscopy of Collisionally
      Cooled Hydrofluorocarbon Vapours.
      KEVIN M. SMITH, GEOFFREY DUXBURY,
      DAVID A. NEWNHAM and JOHN BALLARD.

H 4   Cavity ring down spectroscopy on transient species.
      MARKUS KOTTERER, TOMASZ MOTYLEWSKI,
      HAROLD LINNARTZ and JOHN. P. MAIER.

H 5   A jet FTIR spectrometer for the detection of weak absorption bands.
      MARTIN HEPP, ROBERT GEORGES, and MICHEL HERMAN.

H 6   Molecular beam FT-microwave spectroscopy - Stark effect -.
      DANIELA CONSALVO and WOLFGANG STAHL.

H 7   Ultra-fine Structure in the λ5797 Diffuse Interstellar Absorption Band.
      T.H. KERR, J.R. MILES, R.E. HIBBINS, S.J. FOSSEY,
      P.A. BOICHAT and P.J. SARRE.

H 8 N_2, O_2, and air-broadening coefficients of water vapour.
      J.-M. COLMONT, D. PRIEM and G. WLODARCZAK.

H 9   Photodissociation dynamics of T-Butylnitrite.
       G.R. KENNEDY, C. NING and J. PFAB.

H 10 N_2 Lineshift coefficients in the v_2 water vapour band.
       A. VALENTIN and F. RASHET.

H 11   Complete theoretical analysis of the first decade of the $H_2{}^{18}O$ Interacting vibrational
       states: Line positions and Intensities.
       C. CAMY-PEYRET, J-M. FLAUD, J-Y. MANDIN, A. BYKOV, O.
       NAUMENKO, L. SINITSA and B. VORONIN.

H 12   Line shift Investigations in the v_2 band of H_2S.
       A. KISSEL, B. SUMPF, H-D. KRONFELDT,
       B.A. TIKHOMIROV and YU. N. PONOMAREV.

H 13   A theoretical calculation of the Absorption Spectrum of CH_2^+
       GERALD OSMANN, P.R. BUNKER, PER JENSEN and
       W.P. KRAEMER.

H 14   Spatial Localisation of wave packets composed of many vibrational states.
       N.E. KUZ'MENKO, V.V. ERYOMIN and I.M. UMANSKII.

H 15   Modeling at the *AB INITIO* Limit.
       ATTILA G. CSÁZÁR and WESLEY D. ALLEN.

H16   Rotational Analysis of the Weak Bending Overtones $n\,v_2$ (n=2,3) of the HDS
       Molecule
       O.N. ULENIKOV, E.A. DITENBERG, I.M. OLEKHNOVITCH, S.ALANKO, M.
       KOIVUSAARI and R. ANTTILA

H 17   Coupled Cluster Calculations for three low-lying doublet states of linear C_{10}^-.
       PETER BOTSCHWINA and STEFAN SCHMATZ.

H 18   Conformationally induced rotations of the molecular electronic transition moments
       in substituted Benzenes. A combined experimental and theoretical study.
       I.A. DICKSON, R.T. KROEMER, E.G. ROBERTSON and
       J.P. SIMONS.
       D.R. BORST, J.W. RIBBLETT and D.W. PRATT.

H 19   High resolution Laser spectroscopy of the $^{23}Na^{39}K$ $B^1f®$ state: Perturbation and
       Predissociation near the dissociation limit.
       S. KASAHARA, M. SHIBATA and H. KATO.

H 20   Renner-Teller effect in the $X^2\Pi_{g(3/2)}$ $(v_1, 2^1, 0)$ levels of $CuCl_2$.
       E. BOSCH, P. CROZET, and J.M. BROWN.

H 21   Free jet absorption millimeter wave spectroscopy of complexes of saturated 5-
       Membered rings with argon: 1,3-Dioxolane-Ar and Tetrahydrofuran-Ar.
       G. MACCAFERRI, S. MELANDRI, W. CAMINATI and
       P.G. FAVERO.

H 22 Investigation of the Torsional far-infrared overtones and hot bands of acetaldehyde and interactions with the ν_{10} fundamental bands.
I. KLEINER, N. MOAZZEN-AHMADI, A.R.W. MCKELLAR and J.T. HOUGEN.

H 23 High sensitivity of the rotation spectrum of hydrogen halides in the v=1 state by tunable FIR spectroscopy.
P. DE NATALE, L. LORINI and M. INGUSCIO.
G. DI LONARDO and L. FUSINA.

H 24 Ab Initio study and millimeter-wave spectroscopy of P_2O.
S. BAILLEUX, M. BOGEY, C. DEMUYNCK Y. LIU and ATTILA G. CSÁZÁR

H 25 High resolution FTIR spectrum of the ν_3, ν_4 and ν_5 bands of DCCBr.
ROBERT BROTHERUS, OLAVI VAITTINEN and
LAURI HALONEN. and HANS BÜRGER

H 26 New high resolution analysis of H_2CO in the 3, 6 and 4.3 μm region by Fourier Transform Spectroscopy.
A. PERRIN, J-M. FLAUD, A. VALENTIN, L.R. BROWN.

H 27 An Emission Measurement of Bending Mode Hot Bands of $D^{13}C^{15}N$.
G. Ch. MELLAU, M. WINNEWISSER, S. KLEE
W. QUAPP, M. HIRSCH and A. MAKI.

H 28 High resolution zero-kinetic-energy photoelectron spectra in the 16-20 eV photon energy range
H. PALM, R. SIGNORELL and F MERKT.

H 29 The Intrinsic Torsional Splitting of Ethane.
C. DI LAURO and F. LATTANZI.

H 30 The first stretching overtone of H_3SiD. Emergence of local mode effects.
G. GRANER, O. POLANZ, H. BÜRGER and P. PRACNA.

H 31 High resolution FTIR spectrum of Vinyl Chloride in the 680-1000 cm^{-1} region.
A. DE LORENZI, S. GIORGIANNI and R. BINI.

H32 The detection of very weak rotation-vibration-transitions of $D^{12}C^{14}N$ and $D^{13}C^{15}N$ by tunable diode-laser spectroscopy
R. PETRY, S. KLEE, and M. WINNEWISSER

H 33 Hot bands in the regions of the C-H and C-C Stretching vibrations of HCCl.
A.-M. TOLONEN, T. AHONEN and S. ALANKO.

H 34 High resolution FTIR study of the ν_5 bands of $HSiD_3$, $H^{70}GeD_3$ and $H^{120}SnD_3$.
HANS BÜRGER, WOLFGANG JERZEMBECK,
HELMUT RULAND and LAURI HALONEN.

H 35 Electronic states of scandium monoiodide
E.A. SHENYAVSKAYA, A BERNARD, C. EFFANTIN, F. TAHER, J. D'INCAN, A. TOPOUZKHANIAN, G. WANNOUS.

H 36 Sub-Doppler study of the allowed and $\Delta K = -3$ forbidden Q(3,3) transitions to the v_2 vibrational state of $^{14}NH_3$
H. FICHOUX, M. KHELKHAL, E. RUSINEK, J. LEGRAND, F. HERLEMONT and S URBAN

H 37 Pressure Broadening and Shift of CO_2 Lines Around 1.57 μm.
M. DE ROSA, C. CORSI, M. GABRYSH AND F. D'AMATO

H 38 Laser Optogalvanic Spectroscopy of N_2 from the $A^3\Sigma_u^+$ Metastable State in a Corona Excited Supersonic Expansion
I. HADJ BACHIR, T.R. HUET, J.L. DESTOMBES and M VERVLOET

H 39 Strong Coriolis Coupling Between v_5 and v_{11} States of CH_3CCl_3
Z.KISIEL AND L.PSZCZÓLKOWSKI

H 40 The Electronic Structure of TiCl and TiCl$^+$
C. FOCSA and M. BENCHEIKH

TUESDAY SEPTEMBER 9   9-00

INVITED LECTURES
J
Chairman: J.M. Flaud

J 1   Emission Spectroscopy of the Upper Atmosphere.
      HERMAN OELHAF.

J 2   Hyperfine structures in the Rotational Spectra of Molecular Complexes
      W. STAHL.

TUESDAY SEPTEMBER 9   10-30 to 12-30

POSTER SESSION
K

K 1   Wigner statistic of the nearest distribution of highly vibrational states of CS_2..
      L. MICHAILLE, G. SITJA and J.P. PIQUE.

K 2   IR spectroscopic study of the vibrational-ratational spectrum of N_2O_3 at 1830 cm^{-1}.
      M. SCHERER and M. HAVENITH

K 3   Trace Gas detection of molecules near 3.5 μ using laser difference frequency
      generation.
      N. MELANDER , Y. MINE, K. PETROV, R.F. CURL and F.K. TITTEL.

K 4 H_2O-Ar profiles in the millimeter wave range. Linewidths, Lineshifts and
      Continuum.
      R.R GAMACHE, M. GODON and A. BAUER.

K 5   Measurements and modelling of the line positions and intensities for the H_2S
      molecule in 4500-5500 cm^{-1} (First Hexad) Region.
      O.V. NAUMENKO, L.R. BROWN, L.N. SINITSA and
      M.A. SMIRNOV.

K 6   Setting of a Ti:Sa Spectrometer.
      F. HERREGODTS, M. HEPP, J. VANDER AUWERA and
      M. HERMAN.

K 7   Diagnostic and modeling of N_2O hollow cathode dischages, time-resolved FTIR
      emission studies.
      T. DE LOS ARCOS, C. DOMINGO, A. SCHULTZ and
      I. TANARRO.

K 8   Precise line parameters and cross-sections of the oxygen A band for $O^{16}O^{16}$ and its
       Isotopomer $O^{16}O^{18}$.
       ROLAND SCHERMAUL and RICHARD C. M. LEARNER.

K 9   Intergrated Band Intensities of Chloroform and Fluoroform.
       ROBERT MCPHEAT and GEOFFREY DUXBURY.

K 10   NLTE Effects in the *NO* Fundamental Bands.
       B. FUNKE, M. LOPEZ-PUERTAS, G. ZARAGOZA, G. STILLER, and H.
       FISCHER.

K 11   Vector and Scalar correlations in the 193 nm photodissociation of CH_3COCN.
       S.W. NORTH, A.J. MARR, T.J. SEARS and G.E. HALL.

K 12   Line broadening in the v_2 and v_5 bands of $^{12}CH_3F$ perturbed by O_2.
       JAQUES WALRAND, MURIEL LEPÉRE and
       GHISLAIN BLANQUET. JEAN-PIERRE BOUANICH.

K 13   Line shift in fundamental bands of different Isotopomers of Carbon Monoxide.
       A. KISSEL, O. KURTZ, I. MEUSEL, B. SUMPF, S. VOIGT,
       J.P. BURROWS, J. ORPHAL and H-D KRONFELDT.

K 14   On Isotope effect in the expanded local mode approach: XY_2 (C_2V) molecules.
       O.N. ULENIKOV, I.M. OLEKHNOVITCH and R.N. TOLCHENOV.

K 15   Use of Quantum-Mechanical calculations and rotational analysis to determinate the
       structure of the high energy conformer of 1,3-Butadiene.
       G.R. DE MARE, YU. N. PANCHENKO and
       J. VANDER AUWERA.

K 16   Anharmonic coupling in the overtone spectra of CH_2F_2, CHD_2Cl, CH_2D_2 and C_2D_4.
       M.M LAW and J.L. DUNCAN.

K 17   Theoretical prediction of vibrational states from anharmonic force fields.
       ATTILA G. CSÁZÁR.

K 18   AB Initio calculations for Cyanopolynes $HC_{2n+1}N$ and their Protonated Species.
       P. BOTSCHWINA, A. HEYL, M. HORN, K. MARKEY and
       R. OSWALD.

K 19   Photoionization efficiency spectroscopy of TiO, YO, ZrO and MoO.
       BENOIT SIMARD and HANS PETER LOOCK.
       SARA WALLIN, OLLI LAUNILA and COLAN LINTON,

K 20   Experimental Investigation of Long-Range Interactions in Na_2.
       M. ELBS, T. LAUE, H. KNÖCKEL and E. TIEMANN.

K 21   Bound-Bound and Bound-Free A-X transition of NO-Ar Van der Waals molecule
       studies by laser induced Fluorescence-Preliminary theoretical calculations.
       N. SHAFIZADEH, T. PINO, M. DYNDGAARD, J-H. FILLION,
       P. BRECHIGNAC, D. GAUYACQ, M. RAOULT, B. LEVY and
       J. C. MILLER.

K 22 Time Dependent Quantum Defect Theory Auto-ionisation and Pre-dissociation
      Dynamics
      F. TEXIER and Ch. JUNGEN.

K 23 The Microwave Spectrum of 4,5-Dimethylthiazole.
      A. WELZEL and W. STAHL.

K 24 Rotational Spectrum of Isoxazole-CO.
      SHANE J. MCGLONE and ALFRED BAUDER.

K 25 MW Spectra and Internal Rotation of 1-4 difluoro-2-butyne and two Deuterated
      Species.
      NIELS WESSEL LARSEN, HANNE CHRISTIANSEN and
      MARIE WANDEL.

K 26 Rotational Spectrum of Vinylarsine.
      P. DRÉAN, D. PETITPREZ and S. KASSI J. C. LÓPEZ and J.L. ALONSO.

K 27 Rotational Spectra of NeH$^+$ and NeD$^+$.
      K. TAKAGI and F. MATSUSHIMA.

K 28 The Hydrogen Bonded Complex Pyrazine-H_2O.
      W. CAMINATI, A. MARIS, S. MELANDRI and P.G. FAVERO.

K 29 Study of the Spectra of Silane in the 3000 cm^{-1} region by Fourier Transform
      Spectrometer.
      M. TERKI-HASSAINE, CH. CLAVEAU, A. VALENTIN and
      G. PIERRE.

K 30 Sensitive Overtone Spectroscopy of $2v_1$ of Chloroform ($CHCl_3$) with very High
      Resolution.
      T. PLATZ, W. DEMTRÖDER, H. HOLLENSTEIN and M. QUACK

K 31 The v_1 and v_{22} bands in Pyrrole.
      A. MELLOUKI and M. HERMAN.

K 32 The Rovibrational energy levels in Acetylene ^{12} C_2D_2.
      M. HERMAN, M.I. EL IDRISSI, A. PISARCHIK,
      A. CAMPARGUE, L. BIENNIER, G. DI LONARDO and
      L. FUSINA.

K 33 High-Resolution study of the first stretching ovrtones of $H_3Si^{79}Br$.
      A. CEAUSU, G. GRANER, H. BÜRGER E.B. MKADMI,
      P. PRACNA and W.J. LAFFERTY.

K 34 Absolute line intensities in the $2v_3$ band of $^{16}O^{12}C^{32}S$.
      D. BERMEJO, J.L. DOMENECH, J. SANTOS, J-P. and G. BLANQUET.

K 35 High-Resolution FTIR study of the v_3+v_4, v_1+v_4 and v_1+v_2 rovibrational bands of
      PF_3 between 1100 and 1500 cm^{-1}.
      R. SEBIHI, N. BEN SARI-ZIZI, H. NAJIB and P. PRACNA

K 36 The Lowest Infrared bands of CS_2 with a resolution of 0.001 cm^{-1} for Calibration purposes.
J. PIETILÄ, T. AHONEN, V-M. HORNEMAN, S. ALANKO,
R. ANTTILA, M. KOIVUSAARI and A-M. TOLONEN.

K 37 Global Fitting of CO_2 Vibrational-Rotational line Intensities using the effective Operator approach.
S.A. TASHKUN, V.I. PEREVALOV, J-L. TEFFO, and
V.G. TYUTEREV.

K 38 A Stabilised Scanning High Resolution NIR diode Laser Spectrometer.
T.D. BEVIS and N.J. BOWRING.

K 39 Investigation of Structural Conformers In 4-Pyrrolidinobenzonitrile and Ethyl 4-Pyrrolidinobenzoate and their Clusters with Water and Argon.
J. MCCOMBIE, AND M.J. WALKER. J.P. SIMONS A. HELD AND D.W. PRATT

WEDNESDAY SEPTEMBER 10   9-00

<center>INVITED LECTURES
L
Chairman: P.J. Sarre</center>

L 1   Tracking the Dynamics from Spectroscopic Excitation to Photo-Dissociation.
RICHARD N. DIXON.

L 2   Photoassociation Below 1 mK: A new Light on Molecular Spectroscopy.
PAUL D. LETT.

WEDNESDAY SEPTEMBER 10 10-30 to 12-30

<center>POSTER SESSION
M</center>

M 1   Ozone: First Observations of v_2=3 states through Infrared High Resolution Spectra.
A. BARBE, V. G. TYUTEREV, S. MIKHAILENKO and
J.J. PLATEAUX.

M 2   The structure of Azulene as determined by Fourier transform microwave spectroscopy
S. HUBER and A. BAUDER

M 3   High S/N FT-IR Emission Setup for the Range 300-1100 cm^{-1}.
G.Ch. MELLAU and M. WINNEWISSER.

M 4   An Optimized White-type gas cell for the Bruker IFS 120 High Resolution FTIR
Spectrometer.
T. AHONEN, P. KARHU and V-M. HORNEMAN.

M 5   A FIR laser Magnetic Resonance Spectrometer for Measuring Radicals of
Atmospheric Relevance.
H-W. HÜBERS, L. TÖBEN and H.P. RÖSER.

M 6   Spectroscopy of Carbon Species $C_4 - C_{15}$, $C_4^- - C_{22}^-$, C_{14}^-, C_{16}^-, C_{18}^- and C_{20}^-.
PATRICK FREIVOGEL, MICHEL GRUTTER, DANIEL FORNEY and JOHN P.
MAIER.

M 7   Pressure Broadening and shift coefficients in the $2v_2^0$ and v_1 bands of $^{16}O^{13}C^{18}O$.
V. MALATHY DEVI, D. CHRIS BENNER, M.A.H. SMITH and C.P.
RINSLAND.

M 8   Time resolved measurement of Nitric Oxide in human breath by Faraday LMR
Spectroscopy.
L .MENZEL, P. MÜRTZ and W. URBAN.

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M 9   Line-Broadening parameters in the v_4 and v_3 bands $^{12}CH_4$.
       TONY GABARD.

M 10   Extractions of vibrational distribution functions and rotational temperatures from
       High resolution emission spectra emitted by a non uniform medium.
       P.I. PORSHNEV, J.P. MARTIN and M.Y. PERRIN.

M 11   Study of Vibrational Relaxation of v_3 state of O_3 due to collisions with noble atoms.
       V. ZENINARI, D. COURTOIS, YU.N. PONOMAREV and
       B.A. TIKHOMIROV.

M 12   Collisional processesof C_2H_2 perturbed by Xe: Speed dependant broadening effect on
       the lineshape.
       BENOIT LANCE, GHISLAIN BLANQUET,
       JACQUES WALRAND, JEAN-CLAUDE POPULAIRE and
       JEAN-PIERRE BOUANICH and D. ROBERT

M 13   Global fitting of CO_2 vibrational-rotational lines using the effective Hamiltonian
       approach.
       S.A. TASHKUN, V.I. PEREVALOV, J-L. TEFFO, D. BAILLY, V.G.
       TYUTEREV and L.S. ROTHMAN.

M 14   Supercombination Differences and its applications for the problems of high resolution
       vibration-rotational spectroscopy of symmetric top molecules: CHD_3 Molecule.
       O.N. ULENIKOV, G.A. ONOPENKO, N.E. TYABAEVA and
       S. ALANKO, M. KOIVUSAARI and R. ANTTILA.

M 15   Relations of local and normal mode models in pyramidal XH_3 type molecules.
       J. PESONEN and L. HALONEN.

M 16   Symmetry adapted algebraic approach to molecular vibrational spectroscopy
       A. FRANK and R. LEMUS

M 17   Quantum and Semiclassical calculations of line broadening coefficients for S_0 (J)
       lines of H_2-He and H_2-Ar at high temperatures. Comparisons with experiment.
       M.L. DUBERNET-TUCKEY, P. JOUBERT, J. BONAMY and
       D. ROBERT. X. MICHAUT, R. SAINT-LOUP and H. BERGER.

M 18   A theoretical investigation of hydrogen-bonded complexes of type $NH3...H-C\equiv X$
       ($X=N$, CH, C_3H and $C-CH_3$).
       B. SCHULZ and P. BOTSCHWINA.

M 19   Spectrometry of the Oxygen Molecule Dimer.
       V. VEYRET, B. BUSSERY, R. BACIS, L. BIENNIER,
       A. CAMPARGUE, S. CHURASSY and R. JOST.

M 20   The $B^1\Pi \sim C^1\Sigma^+$ perturbation in KLi studied by high resolution laser spectroscopy.
       V. BEDNARSKA, P. KOWALCZYK. and W. JASTRZEBSKI

M 21   FTS Emission Spectroscopy Application to SiF.
       J.-F. BLAVIER, H. BREDOHL and I. DUBOIS.

M 22 BrCNO as a semirigid bender
THORSTEN FLÖCK, PER JENSEN, JIAN-PING GU, GERHARD HIRSCH and
ROBERT J. BUENKER

M 23 Rotational Spectrum of CH₃OH in the excited C-O Stretching vibrational state.
S. TSUNEKAWA and K. TAKAGI.

M 24 Molecular beam Fourier Transorm Microwave Spectroscopy.
D. PETITPREZ, G. WLODARCZAK, P. DRÉAN and S.KASSI.

M 25 The Rotational Spectrum of BrCNO, an example Quasilinear molecule.
H. LICHAU, W. GILLIES, J.Z. GILLIES, B.P. WINNEWISSER and M.
WINNEWISSER.

M 26 Effects of Electron-spin rotational spectra of weakly-bonded oxygen complexes.
WAFAA M. FAWZY.

M 27 Excited vibrational states of Benzene: High resolution FTIR Spectra and analysis of
some out-of-plane vibrational fundamentals of C_6H_5D.
MARCEL SNELS, A. BEIL, HANS HOLLENSTEIN and
MARTIN QUACK.

M 28 Rotational Spectrum of Amino-Cyclbutane.
L.B. FAVERO and G. CORBELLI.
B. VELINO, W. CAMINATI and P.G. FAVERO.

M 29 The $v_6v_6+nv_9$ Levels of Dicyanoacetylene (NCCCCN).
F. WINTHER and F. HEGELUND.

M 30 HCCH Overtone states by laser induced dispersed fluorescence in the Infrared range.
MARIA SAARINEN, DMITRI PERMOGOROV and
LAURI HALONEN.

M 31 Anharmonic constants and fundamental frequencies of $^{12}C_6H_6$.
E. CANÈ, A. MIANI and A. TROMBETTI.

M 32 $D^2\Sigma^+(v=0,1) \rightarrow A^2\Pi(v=0-3)$ transitions of strontium monoiodide
C. EFFANTIN, J. D'INCAN, A. TOPOUZKHANIAN, G. WANNOUS, A.
BERNARD and E.A. SHENYAVSKAYA

M 33 Infrared Spectrum of H_3SiI in the 330-680 and 1070-1360 cm⁻¹ regions. Accurate
determination of the ground state constants.
JIXIN CHENG and GEORGES GRANER.

M 34 High resolution Raman spectra of Diborane (B_2H_6).
J.L. DOMENECH, D. BERMEJO, J. ORTIGOSO and
W.J. LAFFERTY.

M 35 High resolution FTIR study of the v_4+2v_6 rovibrational band of $CH_3^{79}Br$ between
4870 and 5030 cm⁻¹.
N. BEN SARI-ZIZI and C. ALAMICHEL

M36 Contact Transformations and Determinable Parameters in Spectroscopic Fitting
     Hamiltonians
     MIRZA A. MEKHTIEV and JON. T. HOUGEN

M37 Structural and Conformational Properties of 1,2- ethanedithiol as Studied By
     Microwave Spectroscopy and *Ab Initio* Calculations
     K-M. MARSTOKK and HARALD MØLLENDAL.

M38 High-J Pure Inversion Spectrum of ND_3 in the $v_2=1$ State.
     B.S. DUMESH, V.A. PANFILOV and L.A. SURIN.

WEDNESDAY SEPTEMBER 10 20-00

POSTER SESSION
N

N 1   New Assignments of hot band transitions of CH_3D in the region 900-1700 cm^{-1} and recent results on the analysis of th IR absorption spectrum in the region 1900-3200 cm^{-1}.
A.NIKITIN, J.P. CHAMPION, V.G. TYUTEREV, L.R. BROWN, S. KLEE, G. MELLAU and M. LOCK.

N 2   Observation of new infrared transitions in solid Parahydrogen.
M. MENGEL, B.P. WINNEWISSER and M. WINNEWISSER.

N 3   State-to-state energy transfer of electronically excited $A^2A_1NH_2$ observed by time-resolved Fourier transform spectroscopt in the visible.
R. WILHELM, K. ERMISCH and J. LINDNER.

N 4   The first decade of the interacting vibrational states of the $H_2^{17}O$ molecule: First observation and theoretical analysis.
C. CAMY-PEYRET, J-M. FLAUD, J-Y. MANDIN, A. BYKOV, O. NAUMENKO, L. SINITSA and B. VORONIN.

N 5   Optothermal Spectroscopy of formic acid dimer.
U. MERKER, P. ENGELS and M. HAVENITH.

N 6   Laser velocity modulation and Fourier transform spectroscopy in a $H_2O/D_2O/He$ discharge: Observation of the visible system of HDO^+.
T.R. HUET, B. PINCHEMEL and M. VERVLOET.

N 7   Magnetic susceptibility and electric quadrupole moment of the $\bar{A}^1A_2$ excited state of H_2CS by saturation dip and modr Zeeman spectroscopy.
M. GAMPERLING, M. WAGNER, K. MÖLLMAN and W. HÜTTNER.

N 8   Air and N_2-broadening and shift coefficients in the $^{12}C^{16}O_2$ laser bands.
V. MALATHY DEVI, D. CHRIS BENNER, M.A.H. SMITH and C.P. RINSLAND.

N 9   Line positions, strengths, air-broadening and air pressure-shifts of the (0,0) and (1,0) bands of O_2, $b^1\Sigma_g^+ - X^3\Sigma_g$.
D.A. NEWNHAM, W.J. REBURN and J. BALLARD.

N 10 Pressure-Broadening and Pressure-shifting of spectral lines of ozone.
ROBERT R. GAMACHE, ERIC ARIÉ, CORINNE BOURSIER and JEAN-MICHEL HARTMANN.

N 11 Investigation of J-dependance of line broadening and lineshift coefficients in the v_1+3v_3 band of Acetylene.
H. VALIPOUR and D. ZIMMERMAN

N 12 Monofluorooxirane: Synthesis, High resolution Spectroscopy, structure, IR laser chemical reaction dynamics and AB initio calculations.
JÖRG POCHERT.

N 13 Absolute line intensities in the v_3 fundamental band of Carbon Disulfide CS_2.
GHISLAIN BLANQUET, JACQUES WALRAND and
LAURENT ZANOTTO.

N 14 Correlated and non-correlated lineshape models under small line shift condition application to self-perturbed CH_3D.
BENOIT LANCE, STÉPHANIE PONSAR, MURIEL LEPÉRE, JACQUES WALRAND, GHISLAIN BLANQUET and JEAN-PIERRE BOUANICH.

N 15 Invariant parameters for C_{3v} molecules in the tensorial formalism.
J.P. CHAMPION, A.V. NIKITIN and V.G. TYUTEREV.

N 16 H_3^+ at Dissociation: Potential Energy Surface and Spectroscopy.
RITA PROSMITI, OLEG L. POLYANSKY and JONATHAN TENNYSON.

N 17 Line stengths of torsion-rotation transitions of Methanol for $J \leq 20$ and $v_t \leq 1$, including torsional variation of the dipole moment operator.
MIRZA A. MEKHTIEV, PETER D. GODFREY and JON T. HOUGEN.

N 18 Space Groups, Site Symmetry, Large-Amplitude Motions and Effective Rotational Hamiltonians.
P. GRONER.

N 19 A theoretical study of the hydrogen cyanide dimer.
A. HEYL and P. BOTSCHWINA.

N 20 Infrared diode laser absorption spectroscopy of bound and quaisbound states of HeH^+.
ZHUAN LIU and P.B. DAVIES.

N 21 On the Spin-Orbit Interaction between the Low-lying $^2\Pi_g$ and $^2\Sigma_g^+$ electronic states of $CuCl_2$.
J.M. BROWN, A. YIANNOPOULOU, A.J. ROSS and P. CROZET.

N 22 The v_1, $2v_2$, $2v_3+v_4$ Band System of Carbonyl Fluoride.
MARK J.W. MCPHAIL, GEOFFREY DUXBURY, ROBERT MCPHEAT and RANDY D. MAY.

N 23 The hyperfine structure of AsF_3 in the vibrational state $v_4 = 1$.
H. HARDER, C. GERKE, L. FUSINA and P. DRÉAN.

N 24 High resolution Spectroscopy of Ar-CH_4 and Kr-CH_4 in the 7 µm region (j = 1 ← 0 and j = 0 ← 1 transitions).
D.A. ROTH, M. WANGLER, I. PAK, M. HEPP,
G. WINNEWISSER, D. SCOUTERIS, BRIAN J. HOWARD and K.M.T. YAMADA.

N 25 Microwave spectroscopy of CFC-Halon replacement compounds:
Bromodifluoromathane and 1-bromo-1-fluorothane.
TERUHIKO OGATA, YOSHIO TATAMITANI and
SUSUMA KUWANO.

N 26 Microwave spectrum, ring puckering vibration and AB Initio calculations on 1,1-
Difluorocyclobutane.
A. LESARRI, J.C. LÓPEZ, J.L. ALONSO, G. WLODARCZAK and J.
DEMAISON.

N 27 The molecular Geometry and Hyperfine Coupling Constants of OPF.
BETHANY GATEHOUSE, THOMAS BRUPBACHER and MICHAEL C.L.
GERRY.

N 28 Microwave Spectra of Ethylene Glycol and the Identification of the gGg'-
Conformation.
DINES CHRISTEN, HARALD MØLLENDAL,
ANGELICA H. WALKER, and RICK D. SUENRAM.

N 29 High resolution stimulated Raman spectrum of the ν_2 band of Diacetylene and
associated bands.
J. SANTOS and D. BERMEJO.

N 30 The high resolution infraredspectrum of C_6D_6.
E. CANÈ, A. MIANI and A. TROMBETTI.

N 31 Saturation spectrum of the ν_2 / ν_4 DYAD of AsH_3.
G. SPIEGL and W.A. KREINER.

N 32 Localisation of vibrational energy in $^{120}SnD_4$.
M. HALONEN and L. HALONEN, H. BÜRGER and W. JERZEMBECK.

N 33 Absolute intensity measurements in the 7.5 µm region of Acetylene.
M. EL AZZAOUI and J. VANDER AUWERA.

N 34 High resolution NIR diode laser spectroscopy of Propyne.
T.D. BEVIS and J.G. BAKER.

N 35 Diode laser spectroscopy of cis-1-chloro-2-fluoroethylene in the ν_6 band region.
P. STOPPA, S. GIORGIANNI, S. GHERSETTI and A. GAMBI.

N 36 Vibrational Predissociation in the Vibronic States of Aniline-Neon Van der Waals
Complex: High Resolution Laser Spectroscopy and Dispersed Fluorescence
M. BECUCCI, N.M. LAKIN, G. PIETRAPERZIA, E. CASTELLUCCI, Ph.
BRECHIGNAC, B. COUTANT and P. HERMINE

N 37 Collisional Coupling Between the Stark Components of CH_3F Rotational
Transitions
S.BELLI, G. BUFFA, G. CAZZOLI, L. DORE, V. LEMAIRE and O. TARRINI

N38   Vibrational and Rotational Structure of the Ground State of the CS_2 Molecule at
       High Energies
       H. RING, G. SITJA, J.P. PIQUE AND M.S. CHILD

N39   Rotational Spectra of CH_2I_2 AND CD_2I_2
       E. BIALKOWSKA, Z.KISIEL AND L.PSZCZÓLKOWSKI

THURSDAY   SEPTEMBER 11   9-00

INVITED LECTURES
P
Chairman: A. Trombetti

P 1   Spectroscopy of Jet Cooled Complexes Between Chiral Molecules: A New Method
for Enantiomeric Discrimination.
FRANCOISE LAHMANI.

P 2   Nuclear Spin Conversion in Molecules and High Resolution Spectroscopy.
PAVEL. L. CHAPOVSKY.

THURSDAY   SEPTEMBER 11   10-30 to 12-30

POSTER SESSION
Q

Q 1   Rotational spectra of the Tetrahydrotiophene .. HCl and tetrahydrotiophene .. HF
Dimers.
M.E. SANZ, J.C. LÓPEZ and J.L. ALONSO.

Q 2   A new heterodyne spectrometer with tunable diode lasers: Atmospheric ozone spectra
near 1120 cm^{-1}.
B. PARVITTE, M.E. FAYE and D. COURTOIS.

Q 3   The NO dimer: Jet-cooled, low temperature spectra of the v_1 and v_5 bands; matrix-
isolation study of the far-infrared bands.
P. ASSELIN, P. SOULARD, L. KRIM, A. DKHISSI and N. LACOME.

Q 4   Coaxially oriented beam-resonator arrangement Fourier transform microwave
(COBRA-FTMW) spectroscopy: Line shape and line intensity.
JENS-UWE GRABOW.

Q 5   High-resolution absorption cross-sections of NO_2 at atmospheric temperatures and
pressures in the 12500-42000 cm^{-1} range.
S. VOIGT, J. ORPHAL and J.P. BURROWS.

Q 6 $BrNO_2$ (NITRYL BROMIDE) studied by high-resolution
FT-Spectroscopy.
J. ORPHAL, B. REDLICH, H. GROTHE, D. SCHEFFLER, H. WILLNER, A.
FRENZEL and C. ZETSCH.

Q 7   Near Infra-red Tuneable Diode Laser Absorption Spectrometer using an Astigmatic
Herriott Cell for the detection of the trace gases, CH_4 and N_2O.
I.F. HOWIESON, G. DUXBURY, T.D. GARDINER and P.T. WOODS.

Q 8   Stereocontrol of Reactive Encounters using Polarized Light.
       JAN LEO RINNENTHAL, CHRISTOPH KREHER and KARL-HEINZ GERICKE.

Q 9   Fundamental and first hot bands of $O^{12}C^{17}O$ isotopic variants of Carbon Dioxide.
       C. CLAVEAU, J.-L. TEFFO, D. HURTMANS and A. VALENTIN.

Q 10   Rotational relaxation in the CO_2-He and CO_2-AR mixtures: Energy corrected sudden
       approximation modeling from double resonance spectroscopy and infrared
       absorption.
       A. DROUSSIAUX, B. LAVOREL , G. MILLOT, C. BOULET and J.M.
       HARTMANN.

Q 11   Mixed algebraic models for larger linear molecules: $U(2) \otimes U(3)$.
       M. ABBOUTI TEMSAMANI and S. OSS.

Q 12   Phase choices in the matrix elements of angular momenta, directional cosines and
       symmetry operators.
       GEORG OLE SØRENSEN and NIELS WESSEL LARSEN.

Q 13   Rotational Spectra of Phosphorus Monosulphide up to 1 Thz.
       H. KLEIN, E. KLISCH and G. WINNEWISSER

Q 14   Calculated photoelectron spectra of CCl_2F and H_2NO.
       MATTHIAS HORN and PETER BOTSCHWINA.

Q 15   The 3d formalism and some of its applications.
       V. BOUJUT, F. MICHELOT and J.M. CHAMPION.

Q 16   Laser spectroscopy of the $\bar{A}\,^2\Pi \leftarrow \bar{X}\,^2\Sigma^+$ transition of YTTERBIUM
       MONOACETYLENE.
       HANS-PETER LOOCK, ATTILA BERCES, BENOIT SIMARD and COLAN
       LINTON.

Q 17   The $c\,^3\Sigma^+ - b\,^3\Pi_r$ and $g\,^3\Sigma - b\,^3\Pi_r$ transitions of the SIO molecule.
       I. DUBOIS and H. BREDOHL.

Q 18   Submillimeter Wave Absorption Spectroscopy of the Ar-CO van der Waals
       Stretching Vibration.
       I. PAK, R. GENDRIESCH, F. LEWEN, L.A. SURIN, D.A. ROTH and
       G. WINNEWISSER

Q 19   Tunneling Splitting Patterns in the K = O and 1 Levels of $(CH_3OH)_2$.
       NOBUKIMI OHASHI, CATHERINE L. LUGEZ, FRANK J. LOVAS and JON T.
       HOUGEN.

Q 20   Furan$\cdots$HF, 2,5-Dihydrofuran$\cdots$HF, Tetrahydrofuran$\cdots$HF and
       Tetrahydrofuran$\cdots$HCl.
       F. LORENZO, A. LESARRI, J.C. LÓPEZ and J.L. ALONSO.

Q 21 Effective rotational hamiltonian for Dimethyl Ether: Microwave and mm-wave
      Spectra of ground and two torsional excited states.
      P. GRONER, S. ALBERT, E. HERBST and F.C. DE LUCIA.

Q 22 Millimeter-Wave Spectroscopy and Structure of Chloroform.
      J.-M. COLMONT, D. PRIEM, J. DEMAISON and G. WLODARCZAK.

Q 23 Structural and conformational properties of 1,2-Difluoropropane as studied by
      microwave spectroscopy and quantum chemical computations[1].
      K.-M. MARSTOKK and HARALD MØLLENDAL.

Q 24 Vibration-rotation spectroscopy of the C_2D radical by CO-overtone Faraday-laser
      magnetic resonance.
      C. SCHMIDT, M. WIENKOOP, P. MÜRTZ, M. PERI and
      W. URBAN.

Q 25 Study of Carbonyl sulphide (Including rare Isotopomers) by
      mm-wave, CO_2 sideband, stark and LMDR spectroscopies.
      S. NAIM, T. STRUGARIU, A. FAYT, H. FICHOUX, M. KHELKHAL, J.
      LEGRAND, F. HERLEMONT, L. MARGULES, J. COSLÉOU and J.
      DEMAISON

Q 26 Symmetric amino-wagging band of hydrazine.
      M. KREGLEWSKI I. GULACZYK and A. VALENTIN.

Q 27 Infrared Laser Spectroscopy of Phosphorus Analogues of N_2O.
      I.S. BELL, P.B. DAVIES and P.A. HAMILTON.

Q 28 The High-Resolution IR Spectra of the v_{14}, v_{17} and v_{18} bands of Diborane.
      R.L. SAMS, T. BLAKE and S.W. SHARPE.
      J.-M. FLAUD and W.J. LAFFERTY.

Q 29 The ICLAS overtone spectrum of H_2S above 12200 cm^{-1}.
      LUDOVIC BIENNIER, ALAIN CAMPARGUE, OLAVI VAITTINEN and
      JEAN-MARIE FLAUD.

Q 30 Fourier Transform spectrum of the H_2S Molecule in 5600-6800 cm^{-1} (Second Hexad)
      Region.
      O.V. NAUMENKO, L.R. BROWN, L.N. SINITSA and
      M.A. SMIRNOV.

Q 31 The Jet Cooled FTIR Spectrum of Ethane.
      MARTIN HEPP, ROBERT GEORGES and MICHEL HERMAN.

Q 32 High resolution analysis of the complex symmetric CF_3 stretching Chromophore
      absorption in CF_3I.
      HANS HOLLENSTEIN, MARTIN QUACK, E. RICHARD and
      U. SCHMITT. MARCEL SNELS and HANS BÜRGER.

PROGRAMME   32

Q33   On the Modelling Of IR Absorption in the Far Band Wings of CO_2 Perturbed by
      Rare Gases
      A.A. VIGASIN

Q34   Sextic Centrifugal Distortion Parameters for Near Local Mode Molecules
      O.N. ULENIKOV AND S.N.YURCHINKO

THURSDAY   SEPTEMBER 11   14-00

INVITED LECTURES
R
Chairman: L. Meerts

R 1   High Resolution Optical Spectroscopy In Molecular.
DAVID W. PRATT.

R 2   Applications of High Rydberg Spectroscopy in Chemical Dynamics.
T.P. SOFTLEY.

Abstracts

FIFTEENTH COLLOQUIUM
ON HIGH RESOLUTION
MOLECULAR SPECTROSCOPY

Strathclyde University,
GLASGOW
7 - 11 September 1997

A1

Time-Resolved IR Emission Spectroscopy of Highly Vibrationally Excited Molecules

Hai-Lung Dai
Department of Chemistry, University of Pennsylvania,
Philadelphia, PA 19104-6323, USA

Emission from highly vibrationally excited molecules, initially prepared by electronic excitation followed by internal conversion, during their collisional deactivation, is monitored with 50 ns time-resolution by a FTIR spectrometer. Broad band emission across the IR and near IR regions has been observed from vibrational levels above the electronic excited origin for some small polyatomic molecules, indicating the effect of vibronic coupling in mixing electronic excited states with the high vibrational levels. The energy content of the vibrationally excited molecules at any given time during collisional deactivation can be extracted from their emission spectra, allowing collisional energy transfer rates to be determined. It is found that long range forces dominate in energy transfer from highly excited molecules.

A2

Correlated Electronic Wave Functions for Calculations of Potential Energy Surfaces with High Precision

W. Klopper

Department of Chemistry, University of Oslo, N-0315 Oslo, Norway

The computation of the total electronic (nonrelativistic) energy of a polyatomic molecule becomes a very difficult task if high precision is required. All commonly used computational methods of *ab initio* quantum chemistry expand the electronic wave function in a basis set of antisymmetrized products of one-particle orbitals (Slater determinants). Such expansions, however, are not able to balance the Coulomb singularity for $r_{12} \to 0$ due to the interelectronic repulsion term in the Hamiltonian, and as a consequence, the computed energy converges only very slowly towards the exact solution when the basis set is increased.

One obvious and very successful extension to orbital-product expansions is to include functions that depend on the coordinates of *two* electrons, rather than just one. Very recently, a computational approach for many-electron systems has been developed that employs basis functions that depend explicitly on the interelectronic distance r_{12}.

This new method is discussed and the potential of the method is demonstrated by chemical applications in the field of spectroscopy.

B 1

IMPROVEMENT ON SIGNAL TO NOISE RATIO AND ZERO TRANSMITTANCE LEVEL IN FTS RECORDS

L. Régalia, X. Thomas and A. Barbe
Groupe de Spectrométrie Moléculaire et Atmosphérique
UPRESA-CNRS 6089
UFR Sciences, BP 1039, 51687 REIMS Cedex 2 - France.

Thanks to a new software, interferometric measurements of the Fourier Transform Spectrometer of Reims has been improved.

A special care has been taken to obtain a good zero transmittance[1]. Three types of interferometric corrections have been performed : first on asymmetry of interferograms, secondly on the non linearity of the detectors and last on the non linearity of electronic acquisition. These corrections have given a zero level on spectra better than 0.5 % and allowed intensity measurements with absolute precision better than 2 % without corrections on the zero level in the fitting procedure. We show, for example, a table with intensity measurements for the $2v_1$ band of N_2O compared to the recent literature.

Addition of interferograms has allowed an improvment on signal to noise ratio. Thus, new bands of ozone with very small absorption have been assigned. We show spectra allowing to confirm the improvments on zero transmittance level and on signal to noise ratio.

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[1]: L. Régalia, X. Thomas, A. Hamdouni and A. Barbe, J.Q.S.R.T 57, 435-444 (1997)

38

The REMPI and ZEKE Spectroscopy of some Iodine van der Waals Complexes

D.A. Beattie, M.C.R. Cockett, K.P. Lawley, R.J. Donovan and
N. McLeod

Department of Chemistry, University of Edinburgh,
Edinburgh EH9 3JJ, Scotland.

Rydberg states of the van der Waal's complexes of I_2 with Ar have previously been studied[1,2] by (2+1) mass-resolved resonance enhanced multiphoton ionization (REMPI) spectrocopy. We have extended those studies to the $\Omega = 0$ and 2 5d Rydberg states of the I_2-Kr complex based on the $\omega_c = 3/2$ state of I_2^+. The spectra are all red shifted from the uncomplexed I_2 bands. Anharmonic progressions in the $I_2 \ldots$ Kr van der Waals stretching mode ($\tilde{\omega}_e = 49 \pm 2$ and 47 ± 2 cm^{-1} respectively) have been extrapolated to give the dissociation energy. The $5d; \Omega = 2$ state of $I2 \ldots$ Kr has also been used as the resonant intermediate in a two-colour (2+1') zero kinetc energy pulsed field ionization (ZEKE-PFI) experiment to characterise the $^2\Pi_{3/2,g}$ state of the ionized $I_2^+ \ldots$ Kr complex. An anharmonic progression was again seen ($\tilde{\omega}_e = 55 \pm 2$ cm^{-1}). We also report the first observation of the $I_2 \ldots N_2$ van der Waals complex in a (2+1) mass-resolved REMPI spectrum of the $6s\Omega = 1$ Rydberg state ($\tilde{\omega}_e = 71 \pm 2$cm^{-1}. An empirical potential surface calculation predicts the geometry to be trapzoidal, with probably a linear isomer close in energy - for which there is experimental evidence.

1) M.C.R. Cockett, J.G. Goode, K.P. Lawley and R.J. Donovan *Chem. Phys. Lett.* **214** 27 (1993)

2) M.C.R. Cockett, J.G. Goode, R.R.J. Maier, K.P. Lawley and R.J. Donovan *J. Chem. Phys.,***101** 126 (1994)

B3

Analysis of the Internal Rotation in Ethyl Nitrite with the Help of Molecular Beam Fourier Transform Microwave Spectroscopy

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D-24098 Kiel, Germany

The microwave spectrum of ethyl nitrite shows the presence of three rotational isomers. They correspond to *cis-trans*, *cis-gauche* and *trans-gauche* structures [1]. The rotational spectra of these three isomers have been investigated in the frequency region 7-26 GHz with a Molecular Beam Fourier Transform Microwave Spectrometer (MB-FTMW).

For the *cis-trans* ethyl nitrite a- and c-type and for the *cis-gauche* form a-, b- and c-type spectra have been observed. Due to the internal rotation of the methyl group, some lines were split and the torsional barrier, $V_3(CH_3) = 1082(2)cm^{-1}$ for *cis-trans* and $V_3(CH_3) = 918(10)cm^{-1}$ for the *cis-gauche* form, could be determined.

For the *trans-gauche* form a-, b- and c-type spectra have been observed. The b- and c-type lines show a doubling due to the interconversion between the two equivalent gauche conformers through rotation about the C-O axis. We found the difference between the two lowest energy levels of the torsion around the C-O band axis to be 68(5) kHz.

Furthermore, the rotational, centrifugal distortion, and quadrupole coupling constants and some structural parameters have been obtained from the analysis of spectra.

[1] P. H. Turner, *J. C. S. Farad. Trans. II* **1979,** *75*, 317-336.

B4

COAXIALLY ORIENTED BEAM-RESONATOR ARRANGEMENT FOURIER TRANSFORM MICROWAVE (COBRA-FTMW) SPECTROSCOPY: A CRYOGENIC APPARATUS

JENS-UWE GRABOW, SAMUEL PALMER

Radio and Geoastronomy Division, Harvard-Smithsonian Center for Astrophysics, 60 Garden Street, Cambridge, MA 02138 and Division of Engineering and Applied Sciences, Harvard University, 29 Oxford Street, Cambridge, MA 02138, USA

After the initial experiments of microwave spectroscopy in the time domain [1] the technique was first re-born as a steady gas-waveguide [2] application, but evolved soon into a molecular beam-resonator [3] experiment. During the past years a number of improvements were introduced to the technique. Namely the coaxially oriented beam-resonator arrangement (COBRA) [4] [5] improved the resolution and the sensitivity of the Fourier transform microwave (FTMW) spectrometer.

Our latest effort was the improvement of the COBRA-FTMW sensitivity by reduction of the thermal noise background $P_N = kTRB$, i.e. reducing the 300K room temperature noise to 77K - the temperature of liquid nitrogen. We will present a detailed theoretical background which is needed to approach the expected gain in S/N for a spectrometer operated at temperatures significantly below the thermal environment. The critical issues for the successful completion of the project are radiation coupling, signal amplification, and - most importantly - diffraction and reflection losses occurring in the open design of the Fabry-Perot cavity.

[1] R. H. Dicke and R. W. Romer, Rev. Sci. Instrum. 26, 915(1955).
[2] J. Ekkers and W. H. Flygare, Rev. Sci. Instrum. 47, 448(1996).
[3] T. J. Balle and W. H. Flygare, Rev. Sci. Instrum. 52, 33(1981).
[4] J. U. Grabow and W. Stahl, Z. Naturforsch. 45a, 1043(1990).
[5] J. U. Grabow, W. Stahl, and H. Dreizler, Rev. Sci. Instrum. 67, 4072(1996).

B5

A Supersonic Jet Experiment for IR–Spectroscopy of Small Carbon Clusters

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The spectra of pure carbon clusters, C_n, and carbon containing silicon clusters, $Si_m C_n$, have come to the focus of astrophysical interest. The shells of carbon rich stars show a large variety of carbon and silicon containing clusters.

First gas phase ir–spectra have been published by Saykally and coworkers [1-3]. We present the Cologne tunable infrared diode laser spectrometer which probes the cold supersonic jet of a laser ablation cluster source. A rod of graphite or silicon graphite is vaporised by the uv–light of an excimer–laser at 248nm producing clusters of various numbers of atoms. The high resolution gas phase spectra enable us to determine the size and structure of the clusters by their rovibrational ir–spectra.

1 T.F. Giesen, A. Van Orden, R.J. Saykally, *et al.*, Inrared Laser Spectroscopy of the Linear C_{13} Carbon Cluster, *Science* **265**, pp.756–759 (1994)

2 A. Van Orden, T.F. Giesen, R.J. Saykally, *et al.*, Characterisation of silicon–carbon clusters by infrared laser spectroscopy. The ν_1 band of SiC_4 *Chem. Phys. Lett.* **237**, pp.77–80 (1995)

3 J. R. Heath, R.J. Saykally, The Structures and Vibrational Dynamics of Small Carbon Clusters, *On Clusters and Clustering, from Atoms to Fractals*, P.J. Reynolds (ED.), 1993 Elsevier Science Publishers B.V.

B6

LINE POSITIONS AND AIR BROADENING OF PURE ROTATIONAL

TRANSITIONS OF BrO FROM FTS MEASUREMENTS

G. Wagner and M. Birk

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Bromine oxide, BrO, is involved in depletion of stratospheric ozone and, like ClO, plays an important role in case of perturbed polar chemistry. A satellite submillimeter wave heterodyne limb sounder (SOPRANO) for detection of BrO and other species around 500 GHz is currently planned by the European Space Agency. For a detailed feasibility study as well as a retrieval of concentration profiles the air broadening parameters and their temperature dependence are determined within an ESA-funded study.

BrO was formed in a flow reaction from ozone and atomic bromine. The rotational spectrum between 12 and 28 cm^{-1} was recorded with a Bruker IFS 120 HR spectrometer utilising a White-type multireflection cell. The temperature ranged from -60 to +20 °C, the air pressure was about 20 mb. Gas temperatures were retrieved from relative linestrengths of BrO.

Line positions were determined from a separate measurement at low pressure, leading to an enhanced BrO production. Spectroscopic parameters are compared to those obtained by E.A. Cohen at JPL from submillimeter wave measurements.

B7

LINE INTENSITIES AND SELF-. N_2-, O_2-, AND AIR- BROADENINGS FOR THE 3-0 BAND OF $^{12}C^{16}O$.

N. Picqué. G. Guelachvili,

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CNRS, Université Paris-Sud. Bâtiment 350
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C. Corsi. M. Inguscio

European Laboratory for Non-Linear Spectroscopy (LENS)
Largo E. Fermi, 2
I- 50125 Firenze, Italy.

This work undertaken on the 3-0 band of $^{12}C^{16}O$, is motivated by the lack of spectroscopic standards in the near infrared range between 1 and 2 µm. Part of it, concerned with absolute wavenumbers and self-induced pressure lineshift coefficients has already been submitted for publication. [1]

The intensities reported here are obtained from Fourier transform spectra recorded with the LPMA interferometer.

The same instrument has also been used for the determination of the self-induced line broadening coefficients. In order to reduce the systematic errors, these coefficients were also measured at LENS with a diode laser spectrometer.

N_2-, O_2- and air- broadening coefficients are determined from spectra made only at LENS.

All measurements are at room temperature, with pressure ranges reaching at most 1 atmosphere.

[1] N. Picqué and G. Guelachvili. J. Mol. Spectrosc. submitted.

Observation of the $\tilde{A}^1B_2$-$\tilde{X}^1A_1$ Transition of SiC$_2$ in Carbon Stars.

M. E. Hurst[1], T. Lloyd Evans[2], P. J. Sarre[1]

[1] *Department of Chemistry, The University of Nottingham,*
University Park, Nottingham.
NG7 2RD, England.
[2] *South African Astronomical Observatory,*
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The $\tilde{A}^1B_2$-$\tilde{X}^1A_1$ (Merrill-Sanford) bands of SiC$_2$ are observed in absorption in the 4500-5500 Å spectral region of many N- and J-type carbon stars. Following recent vibrational band analysis of the $\tilde{A}^1B_2$-$\tilde{X}^1A_1$ electronic transition, which used laser induced fluorescence and dispersed fluorescence techniques, extensive SiC$_2$ absorption spectra of a number of stars, including W Pic, RV Tra and T Mus, have been assigned for the first time. Hot bands involving the $\nu_3''=1$ vibrational level (196.37 cm^{-1}) are very strong in typical N-type spectra, but were seen to weaken in T Mus for a time in 1994 indicating that the bands were formed in a cooler region of the photosphere.

The $\tilde{A}^1B_2$-$\tilde{X}^1A_1$ transition has been seen in emission in the spectrum of IRAS 12311-3509, with intensities consistent with the optical excitation of cool gas.

Rotational contour modelling of the absorption and emission bands, for both Si^{12}C^{12}C and Si^{12}C^{13}C, was used to calculate the temperature of SiC$_2$ in these stellar and circumstellar environments.

B9

INTEGRATED ABSORPTION COEFFICIENTS FOR
DIFLUOROMETHANE IN THE
200 - 700 cm^{-1} REGION. THE INFLUENCE OF SAMPLE EMMISION

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In relation to a combined effort in estimating the green house warming potential for freon substitutes a detailed investigation of the IR absorption cross sections for such compounds has been initiated [1] In this connection high resolution (0.03 cm^{-1}) FTIR spectra of difluoromethane have been recorded in the 200 - 700 cm^{-1} region at various temperatures from 213 to 297K in pure sample at 80 mbar and in a 1:10 mixing with air at 200 and 800 mbar total pressure.

A temperature and pressure dependency of individual lines were expected, however it also appeared that the integrated absorption cross sections showed a significant temperature and pressure dependency.

Below 1000 cm^{-1} emission from the sample through the interferometer and back towards the detector (backwards emission) may be an important source of error [2]. For the actual experiment corrections between -5 and 6% on the primary results were necessary. Details of the investigation are presented and the results are discussed.

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B10

PHOTOFRAGMENTATION OF OCIO $(A^2A_2v_1v_2v_3) \rightarrow$ Cl (^2P_J) + O$_2$

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The stratospheric trace gas chlorinedioxide undergoes fast photolysis into the products ClO+O (major dissociation channel) and Cl +O$_2$ (minor dissociation channel). Unfortunately, the reported quantum yields for the Cl-channel are still contradictory. The influence of the initial vibrational states of the $(A^2A_2v_1v_2v_3)$ excited OCIO parent molecule on the contribution of the Cl-channel was investigated applying a two-color pump-probe experiment. The detection of the formed Cl-fragments was feasible using three-photon absorption with subsequent monitoring of the laserinduced vacuum ultraviolet fluorescence. Employing this detection technique the mode-selective quantum yields of Cl-atom formation were determined. The knowledge of the overall Cl-quantum yield emanating from OCIO photodissociation is important in estimating wether chlorinedioxide has an impact on the stratospheric ozone layer.

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B11

Pressure induced line frequency shifts
in the ν_2 band of NH_3.

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We report on NH_3 self induced line shifts measured with an infrared diode laser spectrometer. Experimental determinations were performed in the following way[1]: the diode laser is frequency stabilised on the absorption peak of the line under study; the pressure induced line shifts are then responsible for the laser frequency drifts which are monitored versus the absorbing gas pressure. The measurement reliability is obtained thanks to a frequency discriminator which consists of a reference celll filled with the same absorbing gas set at a fixed pressure.

A number of rovibrational transitions of the ν_2 band of NH_3, involving low J and K values, have been considered: the obtained results allow to discuss the additivity rules for collisional lineshifts[2]

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B12

SELF AND FOREIGN GAS PRESSURE BROADENING AND SHIFT OF THE
aQ(9,9) TRANSITION LINE OF AMMONIA VERSUS TEMPERATURE.

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Lineshape studies of molecular transitions have always been important in basic and applied research. Ammonia, among the molecular species, has been extensively measured not only because it is a component of the atmosphere of Jupiter and of other celestial bodies, and it is also present as a trace gas in the Earth atmosphere, but also because of its large molecular dipole and its singular inversion energy spectrum. The latter properties are important for developing theoretical models which should then be validated against the experimental results. However this much needed procedure has not been perfomed in a satisfactory way up to a few years ago, because pressure broadenings and shifts in ammonia were known with experimental errors usually around 10% and more than 30% respectively, and practically no measurements as a function of temperature were available. This unpleasant situation changed recently, when for a few transitions the errors have been drastically reduced to less than 3% and 10%, respectively [1,2]. Now these measurements have been extended to several other ammonia transitions, and in particular the aQ(9,9) line at 921.255 cm^{-1} has been studied versus temperature also with foreign gases, N_2, O_2, Air, H_2, He, and Ar, as perturbers. The experimental results have shown, to our surprise that the ratio shift/broadening is much bigger in the foreign gas than in the self gas case. As a consequence small values of shifts have been measured with proportionally small errors for the first time. A close comparison with a slightly modified ATC theory has been possible only in the case of self and N_2 pressure effects, because in the other cases the basic approximations of the theory fail. However the experimental data have been fitted by using empirical power laws with a satisfactory agreement.

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B13

THE ROTATIONAL SPECTRUM OF SODIUM TRIMER

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As evidenced by spectroscopic investigations,[1] the ground $\tilde{X}$ and the excited $\tilde{A}$ electronic states of sodium trimer are dominated by Jahn-Teller induced rovibronic effects and can be treated as ordinary asymmetric rotors. This description, however, is only approximate because three effects of similar magnitude,[2] pseudorotation tunneling, spin-rotation, and hyperfine interactions, should also be considered.

In this paper, a theoretical treatment is presented which allows us to treat these three effects simultaneously. The large amplitude pseudorotation tunneling motion is accounted for using an I.A.M.-like approach in which spin-rotation effects are included. This first step yields the rotational dependence of the tunneling splitting which turns out to be in $\cos \frac{2\pi}{3} K_c$. Hyperfine interactions are afterwards included in the treatment. In this second step, symmetry adapted hyperfine functions must be used so that the overall wave function belongs to the symmetry species required by the Pauli principle. At last various hyperfine patterns can be drawn and their dependence on the tunneling symmetry species will be discussed. We hope that these results will be helpful in understanding the complicated patterns observed in various electronic spectra.[2-3]

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B14

ACCURATE CALCULATION OF THE ROTATION-VIBRATION ENERGIES OF HeH$_2^+$ USING RAYLEIGH-SCHRÖDINGER PERTURBATION THEORY

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All bound and some of the lowest quasi-bound ro-vibrational energy levels of HeH$_2^+$ are evaluated within the framework of the Sutcliffe-Tennyson Hamiltonian for triatomic molecules[1] using the Rayleigh-Schrödinger perturbation theory approach developed recently for evaluating nonadiabatic corrections to the adiabatic energy levels of a system of coupled oscillators[2].

Two subsequent adiabatic separation schemes for the vibrational motions are applied to study their effect on the quality of the dynamical calculations. Comparison with full-dimensional, numerically exact calculations shows that a rather high accuracy level is preserved when separating the high-frequency H$_2^+$ stretching motion from the remaining low-frequencies motions. Further separation of the low-frequency motions is less quantitative. However, the corresponding non-adiabatic corrections are accountable fully by means of the perturbation theory.

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B15

SYMMETRIZED LOCAL STATES AND EFFECTIVE DIPOLE MOMENT WITHIN A ROVIBRATIONAL CARTESIAN PICTURE

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Some octahedral molecules, such as SF_6, WF_6 ou UF_6, display a local (or cartesian) behaviour in the excited states of their ν_3 stretching mode. This character may be described through the group chain $U(3) \supset K_3 \supset O_h$ [1].

The preceding theoretical results are extended with:

- the construction of a symmetrized local rovibrational basis, denoted $|n; J_\eta \ |K| \ \Gamma\mu\rangle$, well adapted to the rovibrational study of the $(n00)$ local states of the ν_3 ladder.

- the introduction of an effective dipole moment, with which the infrared intensities for the transitions $(000) \rightarrow (n00)$ with n odd can be computed.

Quite simple expressions are obtained in the symmetrized basis, for the Hamiltonian matrix elements as well as for those of the dipole moment.

This should greatly facilitate the spectral analysis of molecules with a strong local character, especially when the density of states becomes important (high n and J values). As an illustration, preliminary results of simulations made on $^{238}UF_6$ will be presented.

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A DVR STUDY OF THE $\tilde{A}^2B_2 \leftarrow \tilde{X}^2A_1$ ABSORPTION SPECTRUM OF NITROGEN DIOXIDE.

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Using available potential energy surfaces[1] [2] for the two electronic states and their interaction, the $\tilde{A}^2B_2 \leftarrow \tilde{X}^2A_1$ absorption spectrum of NO_2 is investigated. The calculation of the vibronic energy levels, the analysis of the nuclear wavefunctions and the influence of the conical intersection between the two electronic states are studied using a three-dimensional DVR program with two coupled electronic surfaces, to solve the nuclear problem.

Comparison with various experimental data, including high and low resolution spectra are presented.

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B17

HIGH RESOLUTION NEAR INFRARED ELECTRONIC SPECTROSCOPY OF HCBr AND DCBr

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The $\tilde{A}^1A"$ - $\tilde{X}^1A'$ transition in HCBr and DCBr has been investigated using transient frequency modulation (FM) absorption spectroscopy. The (010) - (000) system between 11930 and 12030 cm^{-1} of HCBr and the (020) - (000) system between 12330 and 12400 cm^{-1} of DCBr were recorded. Previous measurements of the (020) - (000) transition of HCBr ($v_0 = 12786$ cm^{-1}) indicate that it is a linear-bent transition,[1] however, in the excited state vibrational levels we examine it appears that the molecule is bent. The levels we investigate, particularly in DCBr, must therefore lie only just below the barrier to linearity. This is borne out by the highly perturbed nature of the energy levels in these excited states and consequently the spectra observed. A barrier to linearity of 1200 to 1600 cm^{-1} above the zero-point energy for the $\tilde{A}^1A"$ has been estimated.

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B18

RYDBERG-VALENCE INTERACTIONS IN THE NEAR-THRESHOLD REGION OF CO.

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Over the past seven years, major efforts aiming at clarifying the near-threshold electronic structure of CO have met with only limited success, the difficulties arising from strong interactions of the Rydberg levels built on the ground state of the ion with core-excited states, and from widespread perturbations of the Rydberg by non-Rydberg valence configurations. New high-resolution jet absorption studies of four CO isotopomers (12-16, 12-18,13-16, 1318) have been carried out at the Photon Factory synchrotron facility in Tsukuba and at the recently constructed pulsed jet expansion apparatus in Meudon. They have been complemented by 1XUV+1UV photoionization-experiments performed at the Laser Center of the Free University in Amsterdam. The results extend the observations of the $3s\sigma$ and $4s\sigma$ $^1\Sigma^+$ states into the region above the strongly avoided crossings with the repulsive branch of the D' $^1\Sigma^+$ valence state potential, [1] and they provide growing experimental evidence for the existence of perturbers[2] that reveal themselves only where they reach into the Franck-Condon allowed region through interactions with Rydberg levels built on $X^2\Sigma^+$ or $A^2\Pi$.

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COMPETITION BETWEEN ORBITAL ANGULAR MOMENTUM AND VIBRATIONAL RESONANCE EFFECTS IN THE SPECTRUM OF NH₂

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The $\tilde{A}\,^2A_1 \rightarrow \tilde{X}\,^2B_1$ electronic transition of the NH_2 free radical is one of those best characterised experimentally. It has been known since the pioneering work of Jungen and Merer and their colleagues (Mol. Phys. **40**, 25-94 [1980]) that it provides an excellent vehicle for studying the interplay between orbital angular momentum effects and vibrational resonances. We have extended the stretch-bender calculation to include the effects of overall rotation and spin-rotation interaction. The suite of computer programs based on this theoretical model is used to calculate the ro-vibronic structure for a range of vibronic states of NH_2, including those in which K_a is very large. The results of these calculations are compared with those recently published using the Carter-Handy-Rosmus method[1] , and also with recent time resolved fluoresence measurements made by Loomis at JILA[2]

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B20

THE PURE ROTATIONAL SPECTRUM OF
$^{84}KrH^+$ AND $^{86}KrH^+$

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Rotational absorption spectra of the krypton hydride ion in its ground electronic and vibrational state have been measured using tunable far infrared radiation. This radiation is generated in a MIM diode mixing the tunable microwave radiation with the difference frequency of two CO_2 lasers. These accurate frequency measurements determine the rotational constants B, D anct H and yield transition frequencies accurate to 40 kHz. By combining the new results with former microwave data on several isotopic forms of $^xKrD^+$ a Dunham analysis can be performed yielding accurate information on the Born-Oppenheimer breakdown parameters.

Previously Unobserved Spin Orbit Components of the $e^6\Pi$ and $a^6\Delta$ Electronic States of FeH

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Using the techniques of dispersed and undispersed laser induced fluorescence, the $e^6\Pi-c^6\Sigma^+$ transition of FeH at 620 nm has been recorded at Doppler resolution. In all the previously characterised sextet electronic states of FeH, only transitions involving the lowest three spin components have been assigned. In this work, we report the characterisation of the fourth spin component of the $e^6\Pi$ state, with $\Omega = \frac{1}{2}$. Assignments were made using lower state combination differences which had been deduced from the previous characterisation of *all* the spin components of the $c^6\Sigma^+$ state.

The $\Omega = \frac{1}{2}$ spin-orbit component of the $e^6\Pi$ state displays considerable Λ-type doubling of its rotational levels. This work has also allowed the fourth spin component of the $a^6\Delta$ state to be accessed through the $e^6\Pi-a^6\Delta$ transition. It is hoped that the fifth and sixth spin components of both the $a^6\Delta$ and $e^6\Pi$ states may be treated in the same way.

Structure of aniline-X (X=Ar, [20]Ne, [22]Ne) from high resolution microwave spectroscopy

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We performed high resolution measurements on aniline, complexed with argon and neon, in the spectral region 1-18 GHz using molecular beam Fourier transform microwave (MB-FTMW) spectrometers, available at the University of Kiel.

The pure a-type rotational spectrum of the aniline monomer modifies to a b–type spectrum in aniline-argon. Both a– and b–type transitions are present in the aniline-neon dimer spectra.

The analysis of data yields accurate rotational and centrifugal distortion constants for the ground vibronic state, therewith supporting theoretical results and analysis of experiments on the electronic excited state S_1 [1] [2] [3]. Information about the influence of complexation on the electronic surrounding of the nitrogen atom is additionally provided by the quadrupole coupling constants.

In order to determine the cluster geometry, the r_0-structure has been calculated and the van der Waals parameters are compared to those obtained for other investigated aromatic molecule–rare gas van der Waals complexes.

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B23

ROTATIONAL SPECTRUM OF CORIOLIS COUPLED

VIBRATIONAL STATES V_7 AND V_9 OF HCOOH

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The two lowest vibrational states $v_7(A')$ and $v_9(A'')$ of formic acid HCOOH (C_s symmetry) are close each other with energy difference 14,5 cm^{-1} and are coupled by strong Coriolis resonance.

96 millimeter wave frequencies measured in the frequency range 250-370 GHz together with the 244 rotational transitions reported in Ref. [1,2] were fitted to the effective Hamiltonian with diagonal blocks taken in the form of both A- and S- reductions. Accurate values of 32 rotational, centrifugal distortion, vibrational energy difference and interaction constants have been determined. To reproduce observed weak and strong local interactions and to fit experimental data within accuracy of measurements the nondiagonal terms up to seventh power of J had to be included into the Hamiltonian.

The r.m.s. deviation of our part of transitions used in the fit is 46 KHz and taken from Ref. [1,2] is 188 KHz .

Model used and obtained results will be discussed.

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B24
The Lowest-Frequency Parallel Fundamental Band ($v_5 = 1 \leftarrow 0$) of CH_3SiH_3

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Hindered internal rotation in symmetric tops offers an excellent opportunity to study rotation-vibration interactions coupling levels that involve large amplitude motion. Methyl silane is perhaps the molecule that has been most thoroughly investigated in this regard. Over the last two decades, several studies have been carried out probing the torsional stack of levels ($v_6 = 0,1,2,3..$) in the ground vibrational state along with the corresponding stack in the lowest-lying degenerate vibrational state ($v_{12} = 1$). With the completion of the most recent works in this series [1], [2], over 2700 frequencies have been fit to within experimental error to yield effective values for 37 parameters, including V_3, V_6, and V_9, the three leading coefficients in the Fourier expansion of the hindering potential. The dominant coupling off-diagonal in v_{12} was the Coriolis interaction between (v_{12}, v_6) = (1,0) and (0,3).

In the current investigation, the data set has been expanded by the high resolution infrared measurement of over 900 lines in the lowest-frequency parallel fundamental band ($v_5 = 1 \leftarrow 0$), and the third stack of levels ($v_5 = 1$, $v_6 = 0,1,2,3..$) has been added to the calculation. The dominant coupling off-diagonal in v_5 is the Fermi-type interaction of (v_5, v_6) = (1,0) with (0,4) and (0,5). Perturbations in frequency as large as 1.7 cm-1 are observed and forbidden lines to upper level ($v_5 = 0$, $v_6 = 5$, $K = 1$) are detected for one torsional sub-level.

The analysis illustrates the importance of including Fermi-type interactions in internal rotor molecules even when large values of $|\Delta v_6|$ are involved. Several torsion-rotation terms included in the earlier two band analysis of the ($v_{12} = 1 \leftarrow 0$) spectrum have now been eliminated. The changes in the leading parameters from their counterparts in the ($v_{12} = 1 \leftarrow 0$) study are shown to agree with the changes predicted by the vibrational contact transformation which implicitly eliminated the ($v_5 = 1$) states from the earlier treatment. Most strikingly, the value of V_6 is shown to arise entirely (within experimental error) from the non-resonant interactions involving the ($v_5 = 1$) state. The implications for the interpretation of the molecular parameters for internal rotor molecules (including asymmetric tops) will be discussed briefly.

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Ar-CO: IR-SPECTROSCOPY AND TEST OF SEMI-EMPIRICAL POTENTIAL ENERGY SURFACES

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Using a new multipass cell we were able to significantly increase the sensivity of our computer controlled diode laser spectrometer for the investigation of van der Waals Clusters in a continous slit jet expansion. This allowed the observation of new high lying van der Waals modes of the Ar-CO complex.

Especially experimental studies of high lying van der Waals modes are interesting, since they probe new parts of the intermolecular potential.
The new observed van der Waals modes still show quite a regular behavior, only slightly perturbed by Coriolis-coupling. It will therefore provide a sensitive test for future *ab initio-* and semi-empirical potential energy surfaces.
Based on our experimental data we have deduced a semi-empirical potential energy surface for the Ar-CO van der Waals complex.
We will present the newest spectroscopic results and the semi-empiric potential energy surface.

B26

INTENSITIES OF INTERACTING BANDS:
ν_2/ν_5 FUNDAMENTALS OF CH₃F.

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Using a tunable diode-laser spectrometer[1], we have carefully recorded 93 individual absorption lines belonging to the ν_2 and ν_5 bands of $^{12}CH_3F$ in the spectral range of 1416-1503 cm⁻¹. We have deduced the experimental strengths parameters by using the equivalent width method.

In order to take properly into account the strong Coriolis coupling between ν_2 and ν_5, the analysis has been made within the dyad system[2]. By fitting the experimental data, we have determined the dipole moment derivatives $\partial\mu/\partial q_2$ and $\partial\mu/\partial q_5$, as well as the first order Herman-Wallis correction in K to $\partial\mu/\partial q_5$.

The values derived for the vibrational band strengths of ν_2 and ν_5 were 2.124(18) and 36.96(12) cm⁻².atm⁻¹, respectively. The intensities were reproduced with an overall standard deviation of 1.44 %, to be compared to a mean experimental uncertainty equal to 1.58 %.

Finally, our results for strengths parameters of ν_2 and ν_5 bands of $^{12}CH_3F$ were compared with previous determinations[3,4,5] which shown rather large discrepancies between them.

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High resolution photoacoustic spectrum of AsH$_3$ (600A$_1$/E) bands

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Abstract

A high resolution spectrum of arsine in the region of 11470-11650cm^{-1} was recorded using a sensitive laser photoacoustic apparatus. Vibration-rotation transitions of the local mode pair of bands (600A$_1$/E) were assigned and the major vibration-rotation parameters were obtained by least-square fitting. The results indicate that the local mode pair of states (600A$_1$/E) are split due to perturbations. The selection rules for the quantum number K break down at high J values. In addition, the intensities of the transitions were estimated by reference to standard water lines.

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The Analysis of the FTIR Spectrum of
trans-CHCl=CHF at 800 cm^{-1}

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High resolution infrared spectra of *trans*-1-chloro-2-fluoroethylene have been recorded using the Bruker IFS 120 HR spectrometer at Giessen. The pressure of the sample gas in a 3-m variable temperature cell was selected in order to have Doppler-limited spectra; the wavenumber ranges selected cover all the fundamental vibrations of the molecule. To minimize absorption from hot bands, the cell was kept at a temperature of 263 K.

The *trans*-CHCl=CHF molecule is an asymmetric top rotor and belongs to the symmetry point group C_s; the 12 fundamental vibrations and their species are $9A'$ and $3A''$. The A' bands are hybrid *ab*-type bands, while the A'' bands present pure *c*-type envelopes. The ν_{11} fundamental centered at $\sim$784 cm^{-1} shows a *c*-type envelope. The rotational structure resembles that of a perpendicular band of a prolate symmetric top, and displays almost equally-spaced ^PQ_K and ^RQ_K subbranches. At present there have been no reported studies of the microwave spectra of *trans*-1-chloro-2-fluoroethylene: *ab initio* calculations indicate that the molecule should have a small dipole moment.

From the rotational analysis of this band, molecular constants for both the ground and the $v_{11} = 1$ states have been determined; the results will be presented together with details of the interpretation.

THE ICLAS SPECTRUM OF $^{12}C_2H_2$ BETWEEN 14300 AND 17500 cm^{-1}

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This study is a part of our systematic investigation of visible absorption spectrum of $^{12}C_2H_2$ [1,2]. Its absorption spectrum has been reinvestigated in the range 14300–17500 cm^{-1} by intracavity laser absorption spectroscopy (ICLAS). We have recorded, at high resloution, about 25 absorption bands, half of them being newly observed. The rotational analysis of the new bands is presented here in details. The vibrational assignment of the excited levels is performed with the help of the cluster model developped by Abbouti Temsamani and Herman [3] at lower energies. The agreement between the predicted and calculated vibrational levels and B_v rotational constants is suprinsingly good at this high vibrational excitation. The inclusion of these new data should however lead to an improvement of the model at high energies.

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[3] M. Abbouti Temsamani and M. Herman, 1995, J. Chem. Phys., 102.

THE CORIOLIS RESONATING DYAD ν_4 AND ν_9 OF $CH_2F^{37}Cl$

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The isotopically ^{37}Cl enriched sample of CH_2FCl has been synthesised to record the infrared spectrum in the range 975-1136 cm^{-1} using a TDL spectrometer. In this spectral region are present two fundamentals: the most intense ν_4 band occurring at 1067.71 cm^{-1} and the weak ν_9 band at 1001.93 cm^{-1}. ν_4 (A' symmetry species) is ascribed to the C-F stretching motion and originates an a/b-hybrid band. ν_9 (A" symmetry species) is related to the CH_2 rocking motion and, besides the expected c-type structure, the band shows an additional, stronger pseudo a-type parallel structure following the selection rules $\Delta K_a = 0$ and $\Delta K_c = $ even. The Coriolis induced parallel component derives its intensity from mixing of the $v_4 = 1$ and $v_9 = 1$ vibrational states. Similarly the perturbation-allowed transitions of ν_9 observed in the ν_4 band region and vice versa derive from the same resonance effect.

In the first step of the analysis the two bands were treated separately; in the last round the rovibrational structure of the entire region investigated has been fitted simultaneously to provide the spectroscopic constants of the two levels with the relative first and second a- and b-type Coriolis parameters. These constants can be used to accurately reproduce the observed spectra within the wavenumber precision of the experimental data.

INFRARED SPECTRUM OF $^{13}CH_3I$ IN THE REGION OF THE FUNDAMENTAL BANDS v_1 AND v_4

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The high resolution infrared spectrum of $^{13}CH_3I$ in the region of the fundamental bands $v_1(A_1)$ and $v_4(E)$ near 3000 cm^{-1} (see the low resolution scan below) have been studied in detail. The spectrum was measured with a Bruker IFS 120 HR Fourier spectrometer in Oulu using an instrumental resolution (due to optical path difference and aperture) matching the Doppler width, 0.0030 cm^{-1}. In addition to the fundamentals, an overtone band $2v_5^0$ and a PAPE band $(v_3+v_5^{\mp 1}+v_6^{\pm 1})^0$ have been identified in the region. A total number of 4614 transitions were assigned.
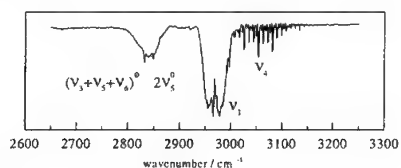
The excited states of these bands, together with $2v_2+v_3, v_2+2v_6^{\mp 2}$, $v_2+v_5^{\pm 1}$, $v_2+v_3+v_6^{\pm 1}$, $2v_5^{\mp 2}$, $(v_3+v_5^{\mp 1}+v_6^{\mp 1})^{\mp 2}$, and $2v_3+2v_6^{0,\mp 2}$ form a complicated level system with a number of resonances coupling the levels. The bands have been analyzed by diagonalizing the complete energy matrices with all the interactions simultaneously taken into account. Our model with 59 free parameters could reproduce the experimental data with only fairly modest standard deviation of 4.4×10^{-3} cm^{-1} (1.2×10^{-3} for the 1839 v_4 lines and 4.5×10^{-3} for the 950 v_1 lines). The physically reasonable values for the parameters were considered more important than just the final standard deviation of the fit. The details of the analysis will be presented.

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HIGH RESOLUTION INFRARED, MICROWAVE AND MILLIMETER WAVE SPECTRA, AND MOLECULAR STRUCTURE OF $SeCF_2$

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$SeCF_2$ is a planar, unstable molecule with a small dipole moment whose spectra are congested by the effect of six Se isotopes. We have synthesized natural and ^{80}Se monoisotopic material and recorded FTIR spectra of $^{80}SeCF_2$ in the region of the fundamentals v_3 (A_1 431.053 cm^{-1}) and v_4 (B_1, 1208.790 cm^{-1}) with a resolution of 3.5 and 2.3 x $10^{-3}cm^{-1}$, respectively. Their analysis yielded ground and excited state rotational constants. Those of the ground state guided the search for pure rotational lines of natural $SeCF_2$ by molecular beam Fourier Transform microwave spectroscopy in the 5 to 26 GHz region and by millimeterwave spectroscopy in the 152 - 240 GHz region. Ground state parameters of the species $^MSeCF_2$, $M =$ 76, 77, 78, 80 and 82, were determined.

Being a fairly heavy molecule with small rotational constants the effective (r_0) should be close to the equilibrium (r_e) structure. Since however isotopic substitution is limited to the Se atom the structural parameters are higly correlated and might be inaccurate. We have therefore confirmed the experimental structure by ab initio calculations at the MP2 level with different basis sets.

Structure of $SeCF_2$ (distances in Å, angle in degree)

	r_0	r_z	r_e[a]	ab initio[b]
r(C-F)	1.3117(1)	1.3123(4)	1.309(2)	1.3050[c]
r(C=Se)	1.7400(2)	1.7420(5)	1.739(2)	1.7330
∠(FCF)	107.64(1)	107.74(4)	107.74(4)	107.69

[a]Extrapolated from the r_z structure.

[b]MP2/6-311G(3df), all electrons correlated.

[c]With offset corrections: r(C-F) = 1.311(2) Å.

B33

STRUCTURAL AND CONFORMATIONAL PROPERTIES OF 1,3-DIFLUOROPROPANE AS STUDIED BY MICROWAVE SPECTROSCOPY AND QUANTUM CHEMICAL COMPUTATIONS[1]

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The microwave spectrum of 1,3-difluoropropane has been investigated in the 10.0 - 36.0 GHz spectral region at dry-ice temperature (-79 °C). Four all-staggered rotameric forms are possible for this compound. The gas phase consists almost exclusively of an equilibrium mixture of two rotameric forms of the molecule denoted GG and AG for which a total of about 2600 transitions have been assigned. The GG rotamer was found to be the most stable conformer and is 4.0(2) kJ mol^{-1} more stable than AG. The dipole moment is lying along the b-inertial axis in the GG conformer for symmetry reasons and is 6.946(29) x 10^{-30} C m. The dipole moment of the AG conformer is (same units) $\mu_a = 3.59(5)$, $\mu_b = 5.32(9)$, $\mu_c = 1.02(19)$, $\mu_{tot.} = 6.50(11)$.

The microwave work has been assisted by *ab initio* computations at the MP2/6-311++G** (frozen core) level of theory, as well as density theory calculations at the B3LYP/6-311++G** level. The structural parameters predicted in both these computational schemes are close to the accurate electron-diffraction values apart from the C-F bond length that is systematically too long. The *relative* energies computed for the different conformers were rather similar at both these levels of theory and in good agreement with experiment.

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HIGH RESOLUTION INFRARED STUDY
OF THE CORIOLIS INTERACTING TETRAD ν_5, ν_3, ν_6, ν_2 in FNO$_2$

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The infrared spectra of the ν_5 (B$_1$, 563 cm^{-1}), ν_3 (A$_1$, 572 cm^{-1}), ν_6 (B$_2$, 742 cm^{-1}) and ν_2 (A$_1$, 822 cm^{-1}) bands of FNO$_2$ have been investigated at resolutions ranging from 0.0023 cm^{-1} to 0.0050 cm^{-1} employing the Bruker IFS 120 HR Fourier transform spectrometer at Wuppertal.

FNO$_2$ is a moderately asymmetric top molecule with an asymmetry parameter κ of +0.50. The molecule is planar belonging to the C$_{2v}$ point group, the C$_2$-axis coinciding with the a-axis.

The fundamentals investigated are the lowest in the molecule. They form a tetrad which is well separated in energy from neighboring levels at higher energies. The four levels interact mutually by a-, b-, and c- Coriolis resonances. The interaction between ν_5 and ν_3 is particularly strong because these levels are close in energy. In this case a $\Delta K_c = \pm 2$ second order c-Coriolis resonance has been identified in the vicinity of $K_c = 20$. For the ν_2 and ν_6 levels Coriolis perturbations are of global nature since no crossings have been observed.

A simultaneous upper state analysis with a four level model based on the Watson asymmetric top Hamiltonian and taking into account Coriolis interactions has been performed. Sets of spectroscopic parameters for the ν_5, ν_3, ν_6 and ν_2 levels as well as improved ground state constants will be presented.

HIGH RESOLUTION LASER PHOTOACOUSTIC AND FTIR SPECTRA OF HCCI

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We have recorded high resolution vibration-rotation spectra of monoiodoacetylene (HCCI) in the wavenumber region 6000 - 13000 cm^{-1}. The photoacoustic measurements above 10300 cm^{-1} have been carried out with a titanium:sapphire ring laser (Coherent 899-21) spectrometer at a Doppler-limited resolution of about 0.02 cm^{-1}. The FTIR measurements, below 9700 cm^{-1}, have been carried out with a Bruker IFS 120 HR spectrometer at a resolution of about 0.01 - 0.0055 cm^{-1}. A multipass cell with an optical path length up to 20 meters has been used in the FTIR studies. Due to the low-lying v_5 fundamental, and due to ro-vibrational resonances the overtone spectrum of monoiodoacetylene shows a rich fine structure. We have found and analyzed nine vibration-rotation bands in the measured region. All the observed bands have been analyzed rotationally producing the rotational constants and band origins for a vibrational analysis. A normal coordinate model with Fermi and Darling-Dennison resonance terms has been applied to provide labels for the high overtone vibrational states of HCCI. By using the model, we have assigned the observed vibrational states. The rotational constants have been reproduced based on the eigenvectors of the calculated vibrational states.

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A COMBINED FIT TO INFRARED AND MICROWAVE SPECTROSCOPIC DATA FOR VIBRATIONALLY EXCITED STATES OF THE KETENE (CH2CO) MOLECULE

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A combined effective rotational constant least-squares fit was carried out for the three lowest vibrational modes of ketene; ν_5, ν_6 and ν_9, using Doppler-limited Fourier-transform infrared data[1] and vibrational satellites from millimetre-wave spectroscopy[2]. In addition some effective constants were obtained also from fits to MMW and FTIR lines in the ν_8 band. The manifestation of Coriolis perturbations in these constants will be discussed.

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176, 133-138 (1996)

B37

OVERTONE SPECTROSCOPY OF ETHYLENE

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We have recorded the slit-jet cooled overtone absorption spectrum of ethylene $^{12}C_2H_4$ between 3000 and 7000 cm^{-1}, at a spectral resolution of 0.02 cm^{-1}, using a Fourier transform interferometer[a]. 12 bands are observed, some not reported before. They are all vibrationally identified and for the first time rotationally analysed. Effective rovibrational constants have been determined for all vibrational levels observed in this work. Anharmonic and Coriolis-type perturbations are considered. Additionally, relative band intensities were estimated. The vibrational energy pattern in ethylene is discussed.

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[a] R. Georges, M. Bach and M. Herman, *Mol. Phys.*, **90,** *381 (1997).*

74

ANALYSIS OF NUCLEAR QUADRUPOLE STRUCTURE IN FTMW SPECTRA OF $^{14}N_2\cdots H^{35}Cl$ AND $^{14}N_2\cdots H^{37}Cl$

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The rotational spectrum of the weakly bound dimer between $^{14}N_2$ and HCl exhibits complex hyperfine splitting patterns due to three non-equivalent quadrupolar nuclei. Determination of coupling constants for all nuclei provides a rare opportunity of deriving information about the effect of intermolecular interaction on both molecules in the dimer. N 2 HCl was first observed by M BER spectroscopy[1], and the DCl isotopomers have been investigated by cavity FTMW spectroscopy.[2]

In the present work we have used the newly commisioned molecular beam, cavity FTMW spectrometer in Warsaw, to determine all three nuclear quadrupole coupling constants for $^{14}N_2\cdots H^{35}Cl$ and $^{14}N_2 \cdots H^{37}Cl$ The difference between the nuclear quadrupole coupling constants for the two nitrogen nuclei has been successfully rationalised by electric field gradient calculations. The flexible data processing system used in the spectrometer and the graphical display programs used to identify the hyperfine components with greatest sensitivity to $\chi(N1)-\chi(N2)$ are described. N $_2\cdots$HCl has been observed on several occasions as an impurity in work involving complexation with HCl and it might have conceivable atmospheric implications. For this reason tables of calculated hyperfine components for two of the most common isotopomers at frequencies 2-18 Ghz are available on request.

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B39

APPLICATION OF A MODULAR DIFFERENCE FREQUENCY SPECTROMETER WITH TWO DIODE LASERS AS PUMP SOURCES FOR TRACE GAS DETECTION AT SUB-PPM-LEVEL

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A modular diode laser-diode laser difference frequency spectrometer designed for multicomponent trace gas detection and high resolution spectroscopy will be presented. A vis diode laser (690 nm) and a nir diode laser (806 mn) are combined in a non-linear crystal (40 mm long, $AgGaS_2$). With an input power of about 6 mW and 20 mW, respectively, an output power larger than 100 nW could be achieved. The systems can cover with one pair of diode lasers a wavenumber range of 21 cm^{-1} near 2100 cm^{-1}. From our measurements an overall resolution better 30 MHz could be estimated. These features allow high resolution spectroscopy as well as trace gas detection of CO under background conditions. After previous studies[1] the system is now capable to measure continously CO-concentrations down to 150 ppb with a temporal resolution below 30 seconds. This will be illustrated by 24h measurements under urban conditions in the centre of Berlin. Moreover, high resolution experiments were carried out for several lines of different isotopomeres of carbon monoxide. As example, line broadening measurements for the R(2)-line of ^{13}CO will be presented. The project is supported by the "Bundesministerium für Bildung und Forschung" and "Verein Deutscher Ingenieure". B. Sumpf acknowledges a grant by the "Deutsche Forschungsgemeinschaft".

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Appl. Phys. B. 64, 521-524 (1997)

Doppler-free Two-photon Absorption Spectroscopy of $A\ ^1A_u \leftarrow X\ ^1A_g$ Transition of $Trans$-glyoxal

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Ultrahigh-resolution spctrum of the $A\ ^1A_u(v_7 = 1) \leftarrow X\ ^1A_g$ $(v = 0)$ transition of $trans$-glyoxal(CHOCHO) has been observed using the technique of Doppler-free two-photon absorption spctroscopy with a single-mode Ti:sapphire laser and a Fabry-Perot enhance cavity. The resolution was $0.00005\ \mathrm{cm}^{-1}$. Rotational lines are fully resolved and the relative transition energy was calibrated by the flinge marks of a stabilized etalon with accuracy better than $\pm 0.0001\ \mathrm{cm}^{-1}$. The observed 1809 lines (mainly Q transitions) were assigned unambiguously and the rotational constants were accurately determined by a least-squares fitting of eigenvalues of the A-reduced Hamiltonian.

We found several lines with energy shifts, intensity anomalies, and line splittings. The spectral feature was remarkably changed with the external magnetic field. It indicates that these are originated from perturbation with vibronic levels of the triplet state $(a\ ^3A_u)$. The line splittings are attributed to hyperfine structure of the ^{1}H$(I = 1/2)$ atoms in the triplet state. We discuss the rotational structure of the $A\ ^1A_u(v_7 = 1)$ state and the mechanism of the singlet-triplet perturbation.

Spectroscopy of interstellar molecules in laboratory and space

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Observations of molecular species by radio telescopes provide important information about physical and chemical properties of interstellar clouds. By using Nobeyama 45-m radio telescope, we are observing various molecular sources in the frequency region of 9-115 GHz. So far a spectral survey observation of a circumstellar envelope of IRC+10216 has been reported on the 28-50 GHz region[1]. In observations of the dark cloud TMC-1 (Taurus Molecular Cloud-1), more than 450 lines were detected in the 9-50 GHz region, and 35 molecular species have been identified. During the survey observations, several new species were identified and summarized in this paper. Since the cloud has low temperature of 10 K and the line widths are narrow as 0.6 km s^{-1} (correspond to 60 kHz at 30 GHz), these measurements contribute to determination of accurate molecular constants of observed species. The results on carbon chain radicals will be reported. So far about 100 molecular species have been identified in interstellar clouds. However, more than 1000 unidentified lines have been reported in radio frequency region. Laboratory spectroscopy has been applied for these unidentified lines by considering chemical reactions of interstellar clouds, and recent results will be presented.

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C2

MILLIMETRE WAVE SPECTROSCOPY OF MOLECULAR IONS

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Since the pioneering work of Woods in 1974 on the rotational spectrum of CO^+, about 25 molecular ions have been studied by microwave and millimetre wave spectroscopy using a d. c. glow discharge as ion source.

From the rotational spectrum of different isotopomers, information on the molecular structure of these reactive species can be derived, as was done in our laboratory, for instance, for species of astrophysical importance like protonated cyanogen and protonated formaldehyde.

In addition to the study of the ground state spectrum, rotational lines in excited vibrational states were detected for isotopomers of the formyl ion, and its equilibrium structure was derived after a careful analysis of a vibration-rotation interaction which affects the spectra.

A rather unexplored but interesting field is the study of the collisional relaxation of the rotational lines of molecular ions. Recently, measurements on HCO^+ perturbed by neutral gases have been carried out, leading to the determination of pressure shift and pressure broadening coefficients. These results allow to have an insight into the dynamics of an ion colliding with a neutral perturber.

LASER VELOCITY MODULATION SPECTROSCOPY OF TiCl$^+$
OBSERVATION OF THE A$^3\Delta$(3d^2) STATE AND
DEPERTURBATION OF THE X$^3\Phi$ - A$^3\Delta$ COMPLEX

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The absorption spectrum of TiCl$^+$ has been recorded in the range 17200-18400 cm^{-1} with a single mode dye laser associated with a velocity modulation detection technique, in an ac glow discharge exciting a gas mixture of He/TiCl$_4$. The high sensitivity of this method allowed the observation of weak forbidden intercombination bands and the resulting determination of the spin-orbit parameters for both the [17.8] $^3\Delta$ and X$^3\Phi$ states, in addition to accurate determination of the rotational constants of the two states, for the two isotopomers Ti^{35}Cl$^+$ and Ti^{37}Cl$^+$ [1].

The analysis of the remaining headless bands led to the identification of the low-lying A$^3\Delta$ state. The v=0 vibrational level perturbs strongly the v=1 level of the X$^3\Phi$ ground state; this gives rise to chaotic values of the effective rotational parameters in both levels. The $\Delta\Omega$=0 spin-orbit effect is responsible of the major part of this perturbation that mixes the X$^3\Phi_3$ (v=1) level with the A$^3\Delta_3$ (v=0) one and the X$^3\Phi_2$ (v=1) level with the A$^3\Delta_2$ (v=0) one. Also the proximity of these levels (always less than 100 cm^{-1}) makes necessary the use of more refined J-dependent effects.

A very acute and peculiar perturbation due to closeness (less than 10 cm^{-1}) is observed between the X$^3\Phi_2$ (v=1) and A$^3\Delta_1$ (v=0) states. It is explained by the spin-uncoupling mixing of the A$^3\Delta_1$ (v=0) and A$^3\Delta_2$ (v=0) states and the spin-orbit interaction between the A$^3\Delta_2$ (v=0) and X$^3\Phi_2$ (v=1) states. It gives rise to a beautiful example of avoided crossing.

All of the 2860 identified lines of the Ti^{35}Cl$^+$ spectrum have been simultaneously fitted through a direct approach 18x18 matrix handling leading to the determination of a set of deperturbed parameters for the three electronic states.

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[1] C. Focsa *et al.*, J. Chem. Phys. **106**, in press (1997)

D2

CONTRIBUTION TO THE ANALYSIS OF THE $^3A_2 \leftarrow X^1A_1$ WULF TRANSITION OF OZONE BY HIGH RESOLUTION FOURIER TRANSFORM SPECTROMETRY

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High resolution absorption spectra of the Wulf bands of ozone have been recorded in the range 8600 - 11200 cm^{-1} at room temperature and -50°C. The best instrumental resolution was 0.020 cm^{-1} with apodisation. Three extremely congested rovibrational bands have been obtained, one of them (hot band) disappearing at low temperature.

Within a near symmetric top model and a coupling case b, we will give an analysis of the 2_0^0 band and the first spectroscopic constants for the vibrational (0,0,0) level of the excited $^3A_2$ state. Due to predissociation processes, the F_2 and F_3 lines are broadened and their positions often difficult to measure. In particular, the highest J lines of the F_2 ^QQ branches show a broadening increasing with J and the K"=11 F_2 subband is not observed. In addition, large distortion constants are obtained in the fits. We will discuss the existence of perturbations and consequences for the lifetime of this bound metastable state, which might play an important role in the ozone cycle models.

D3

INFRARED DIODE LASER SPECTROSCOPY OF THE
$A\ ^2\Pi_u \leftarrow X\ ^2\Sigma_g^+$ SYSTEM OF THE Si_2^- ANION

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The infrared electronic transition $A\ ^2\Pi_u \leftarrow X\ ^2\Sigma_g^+$ of the Si_2^- anion has been investigated using diode laser velocity modulation spectroscopy. Si_2^- was generated in an air cooled low pressure silane and hydrogen discharge. Two vibronic bands $(v',v'')=(1,0)$ and $(2,0)$ have been observed in the frequency range of 670 to 810 and 1200 to 1340 cm^{-1}. One hundred and thirty lines were fitted to standard Hamiltonians, giving accurate molecular parameters for Si_2^-. The determined molecular constants were used to derive some equilibrium parameters of the $^2\Pi$ state. The equilibrium parameters and fine structure constants were compared with previous low resolution experimental results and *ab initio* calculations.

Transient Line Narrowing

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The ultimate limit in spectroscopy is given by the limited interaction time between the molecule and the probing radiation. An novel effect will be presented which reduces the line width of an absorption to well below the limit imposed by the *average* interaction time. For transit broadened transitions it will be demonstrated that transient line narrowing can reduce the line width of a transition by a factor of five whilst even increasing the signal to noise ratio. Using the Cambridge 10μm CO_2 laser spectrometer absorptions in SF_6, normally having a transit limited half width of 14 kHz, have been recorded with a width of only 1.9 kHz. The effective temperature of the molecules participating in the signal was 3 mK in a gas of ambient temperature. This is especially important for meterological applications since the second order Doppler effect is practically eliminated and pressure shifts are greatly reduced.

A simple theoretical model describing the narrowing process in homogeneously broadened transitions will be presented along with an extensive experimental examination.

Some of the technical advances in laser stabilisation necessitated by the much increased resolution will also be described.

The rotational spectrum of the AsH_2 radical in its $\tilde{X}^2B_1$ state studied by far-infrared laser magnetic resonance.

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The rotational spectrum of AsH_2 in its ground $\tilde{X}^2B_1$ state has been recorded using a far-infrared laser magnetic resonance spectrometer.

AsH_2 was first detected by the observation of its optical spectrum[1] and approximate rotational constants were determined. There is a considerable need for refinement of these parameters, both to define the molecular geometry and to help with the analysis of the infrared spectrum of the molecule. AsH_2 is an asymmetric rotor, but close to the oblate top limit, and the allowed rotational transitions are expected to be b-type.

The free radical AsH_2 was formed in the intracavity cell of the spectrometer by the reaction between fluorine atoms and arsine, AsH_3. FIR laser lines with frequencies close to the transition frequencies calculated from the previously determined parameters[1] were scanned. Hyperfine splittings from both ^{75}As and ^1H nuclei were observed: the spectra consist of quartets of triplets (*ortho*) or singlets (*para*). Rotational transitions due to AsH_2 have been assigned, and the data fitted by a least-squares procedure using a computer program in order to determine molecular constants.

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D6

A new Molecular Beam Fourier Transform Microwave Spectrometer for the Investigations of Transient Molecules

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Since the construction of the first pulsed Molecular Beam Fourier Transform Microwave (MB-FTMW) spectrometer reported by Balle and Flygare [1] in 1981, many modifications and improvements were introduced in order to make this kind of spectroscopy more sensitive and also suitable for special applications such as microwave double resonance, laser ablation, and Stark spectroscopy.

We report on a new design for a Molecular Beam Fourier Transform Microwave spectrometer in the spectral region 8 to 18 GHz, especially constructed for the investigations of rotational spectra of radicals, which are produced by UV-laser photolysis of stable molecules by crossing the output from a pulsed KrF excimer laser with the molecular beam. The spectrometer incorporates a Fabry-Perot microwave cavity located in a vacuum chamber. The cavity consists of a spherical and a flat mirror in a near semi-confocal configuration with the cavity resonance being adjusted by movement of the spherical mirror. A piezo actuated pulsed nozzle valve is mounted near the center of the flat mirror, just above the microwave antenna. This provides an expansion along the cavity axis, which produces higher sensitivity and resolution than an expansion perpendicular to the cavity axis [2].

First results will be reported.

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D7

DIODE-PUMPED TERAHERTZ PHOTOMIXING SPECTROMETER

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We have build a high-resolution terahertz spectrometer by mixing near-infrared diode lasers in a fast low-temperature-grown (LTG)-GaAs photoconductor with submicron interdigital electrodes feeding a broadband complementary spiral antenna which radiates the coherent terahertz beat through a sample gas cell to a hot-electron InSb bolometer. The fixed-tuned laser is a single frequency (λ = 852 nm) distributed-Bragg-reflector (DBR) GaAlAs diode, self-locked to a confocal interferometer; and the tunable diode laser is a broadband quantum-well (828 nm < λ < 858 nm) single-mode Littman-Metcalf external-cavity oscillator and a tapered planar amplifier, with precision linear piezoelectric tuning of up to 60 GHz and complete spectral coverage from 0.1 to 2 THz. Sample spectra will be given.

D8

AN ABSORPTION MODULATION TECHNIQUE IN A SUPERSONIC JET USING AN OPTICAL SCANNING SYSTEM ANALYSIS OF THE v_5 BAND OF CHCl₃.

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We have developed a modulation technique which enhances the sensitivity of a infrared diode laser spectrometer for cold jet spectroscopy It consists in spatially scanning the molecular jet with the probe laser beam by the use of a mirror placed on a galvanometric deflector vibrating at a I 1 kHz frequency.

The detection of $^{15}NH_3$ transitions at natural abundance demonstrates the sensitivity of the technique. It can be used in various experimental conditions, and seems to be a good alternative to pulse valve modulation.

As an application we have considered the $CHCl_3$ spectrum. The molecular jet was obtained by flowing argon over heated liquid chloroform before expansion thorough a circular nozzle. About hundred transitions were measured and analysed in region of the v_5 band center at 13 μm.

Maximum Entropy Processing of Fourier Transform Spectra:
Applications to Atmospheric Remote Sensing

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The detection and measurement of small signals in spectra recorded using high resolution Fourier transform spectrometers is often limited by effects other than simple noise. For example non-uniform baselines and drift of baselines in absorption spectroscopy are often an order of magnitude larger than noise levels and thus can severely limit quantification and peak detection. Similarly, sinc oscillations in the baseline, which arise when the interferogram signal has not decreased below the (detector) noise level at the maximum optical path difference, can easily be on the order of a few percent and obscure weak features.

This work describes a post-acquisition method of interferogram processing which very significantly reduces sinc oscillations in Fourier transform spectra without the loss of resolution and allows for simultaneous baseline correction, as shown in HCl test spectrum below. Significant improvements in detection limits and peak position accuracy are achieved. The use of a maximum entropy approach to this problem means a minimum amount of *a prior* information is needed. This method has allowed the direct spectroscopic detection of HBr in far-infrared emission spectra of the stratosphere for the first time.

D10
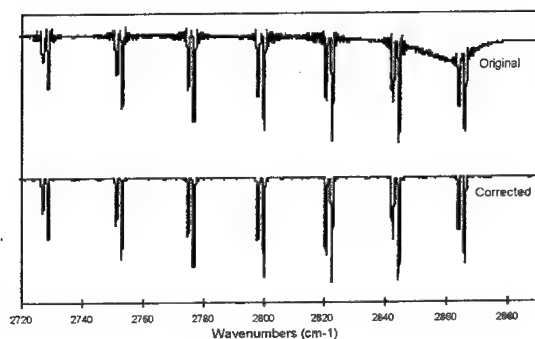
THE VISIBLE ABSORPTION SPECTRUM OF SiH_2 : DENSITY DETERMINATION IN A DC DISCHARGE AND SPECTROSCOPY

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Two high sensitive and quantitative techniques have been applied to the detection of SiH_2 in a DC discharge : the new method of CW Cavity Ring Down Spectroscopy (CW-CRDS) and the Intracavity Laser Absorption Spectroscopy technique (ICLAS). Doppler limited absorption lines of the $\widetilde{A}\ ^1B_1\ (020) \leftarrow \widetilde{X}\ ^1A_1\ (000)$ transition around 580 nm could be observed. The rotational assignment and calculation of the Hönl-London factor of some lines were performed on the basis of the rotational constants obtained by Dubois [2]. From the knowledge of the electronic transition moment obtained from fluorescence lifetimes [3], we have calculated the concentration of SiH_2 in the discharge to be about $7.10^9/cm^3$. Taking into account the signal to noise ratio, concentrations as small as $10^7/cm^3$ can be detected by both methods.

The ICLAS spectrum of the $\widetilde{A}\ ^1B_1\ (000) \leftarrow \widetilde{X}\ ^1A_1\ (000)$ transition has been recorded between 15300 - 16100 cm^{-1}. We hope to be able to present a preliminary rotational analysis of this newly observed transition.

The present study examplifies both the advantage of CRDS which allows to record easily a narrow spectral range with a very high resolution (some MHz) and the advantage of ICLAS which is well suited for a larger coverage of the absorption spectrum with a lower resolution (typically 1 GHz).

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     J. Chem. Phys. 96 (1992) 44.

D11

CALCULATING H_2O STATES UP TO DISSOCIATION STATES USING PDVR3D

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Even small chemically bound molecules have 10^5 or more bound states. Calculations of this size are therefore a grand challenge to conventional computers. So we have parallelized DVR based program suite DVR3D [1] to give PDVR3D [2]. The PDVR3D suite run on the Cray T3D at Edinburgh University and the IBM SP2 at Daresbury.

As a first application of PDVR3D, we are studying the water molecule using two newly available global potentials due to Varandas,[3] and Ho and Rabitz.[4] We have calculated the vibrational levels of water up to dissociation limits for both potentials.

We will present both the vibrational and rotational results at the conference.

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D12

High temperature rotational transitions of water in sunspot and laboratory spectra

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Assignments are presented for hot spectra of water obtained in absorption in sunspots ($T \sim 3000$ °C and $750 \leq \tilde{\nu} \leq 1010$ cm^{-1}) and in emission in the laboratory ($T \sim 1550$ °C, $370 \leq \tilde{\nu} \leq 930$ cm^{-1}). These assignments [1] are made using variational nuclear motion calculations based on a high level *ab initio* electronic surface and with allowance for both adiabatic and non-adiabatic corrections to the Born-Oppenheimer approximations. Some 3000 out of the 4700 transitions observed in the laboratory spectrum are assigned and some 1300 transitions observed in the sunspot spectrum, including all the strong transitions. These transitions mostly involve high lying rotational levels within the (0,0,0), (0,1,0), (0,2,0), (1,0,0) and (1,0,0) bands, for which the energy range of observed levels are approximately doubled. Transitions within (0,3,0), (0,4,0), (1,1,0), (0,1,1), (0,2,1), (1,1,1), (1,2,0) and (1,0,1) are also assigned. For most bands the range of K_a values observed is significantly extended, usually doubled. New features observed include some cases where strongly degenerate levels with high K_a are split by Coriolis interactions. Comparisons are made with the recent linelist of Partridge and Schwenke [2]

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D13

COLUMN DENSITY MEASUREMENTS AND PROFILE RETRIEVAL
OF STRATOSPHERIC TRACE SPECIES USING AN AIRBORNE FTIR.

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As part of the Instruments for Field Measurements in the Atmosphere(IFMA) programme supported by NERC, the equipment required to fly a high resolution FTIR spectrometer (Bruker 120M) was developed. Test flights of the instrument in the Cranfield Jetstream aircraft, produced several sets of high resolution spectra. Observations were targeted on trace species involved in stratospheric chemistry. These data were first reduced using standard ground based techniques. This involved obtaining Column densities for species of interest. As part of R.C.KIFT's PhD new retrieval methods were used to obtain vertical profile information about the relevant species by using the information contained in the lineshape. The results show that even in the difficult measurement environment of an aircraft reasonable results are obtainable.

D14

**A secondary frequency standard from 776 nm to 815 nm
with the iodine molecule**

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The simple physical model of a vibrating rotator, which is used for the description of the level structure of diatomic molecules, allows the calculation of transition frequencies from a limited set of precisely known Dunham parameters. These can be derived from a few highly precise measurements of absolute and difference frequencies, and will be applied for the interpolation of many accurate frequencies adequate as references. We demonstrated[1], that it is possible to stabilize the frequency of a spectrally narrowed diode laser to hyperfine components of the I_2 B 0^+_u - X $^1\Sigma^+_g$ system in the near infrared at a level of stability $\delta v/v \approx 5*10^{-11}$. We investigated systematically the dependence of the hyperfine parameters on the vibrational and rotational quantum numbers. The rotational structure was determined from the beat frequencies of two lasers stabilized of different rovobronic lines, and with the method of bisecting frequency intervals by four-wave mixing in a laser diode[2]. Absolute frequencies of selected hyperfine components of different rovibronic transitions were measured by interferometric wavelength comparison with known laser wavelengths and by frequency comparison either with calibrated Rb atomic lines or with the difference frequency between a Ca standard[3] and a CH_4 standard[4]. About 1000 calibrated frequencies with average separation of 10-20GHz will finally be available by a simple interpolation algorithm with an accuracy of $\delta v/v < 3*10^{-10}$ in the wavelength range given above. The state of the investigations will be reported.

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D15

Photodissociation of CHBr$_3$ at 193 nm and 248 nm: Observation of the electronically excited CH(B $^2\Sigma$, A $^2\Delta$) fragment

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The multiphoton dissociation of CHBr$_3$ is investigated in a supersonic jet with radiation from an excimer laser at 351 nm, 248 nm and 193 nm. In the latter two cases the electronically excited fragment CH is observed in its A $^2\Delta$ and B $^2\Sigma$ states. Time-resolved fluorescence spectra are recorded both with a monochromator/ gated integrator arrangement and by time resolved Fourier transform emission spectroscopy. The dissociation process is discussed in terms of the rotational distributions of the fragment CH and the order of the multiphoton dissociation. The results are compared with multiphoton dissociation from other halogen hydrocarbons and alcohols which have an open dissociation channel to electronically excited CH.

D16

HIGH RESOLUTION INVERSE RAMAN SPECTROSCOPY OF SUPERSONIC EXPANSIONS OF N_2, CH_4 AND MIXTURES WITH He AND Ar.

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A systematic study of rotational relaxation in supersonic expansions of pure N_2 , CH_4 and mixtures with He and Ar has been performed including several detection techniques: Inverse Raman Spectroscopy to determine rotational temperatures, time-of-flight measurements of terminal velocities and mass analysis to monitor complex formation. A broad pressure range was used, along with several nozzle geometries and gas compositions.

In this communication we present an analysis of these measurements focusing on the angular properties of the jet through the analysis of High Resolution Raman lineshape and population distribution among rotational levels, for expansions through a circular pulsed nozzle.

Collinear laser beams were used for CH_4 and near collinear configuration for N_2. Under these conditions, our technique is closer to line-of-sight probing, like IR absorption, than to spatially resolved measurements, and the perpendicular distribution of temperature and density in a direction perpendicular to the axis of the expansion is probed at once.

A detailed model for the observed lineshape in this complex system has been developed, aimed at the analysis of the flow properties in the jet, especially in the region close to the nozzle, where collisional broadening plays a major role besides the usual lineshape due to Doppler shift and strong temperature and density gradients.

PURE ROTATIONAL RAMAN LINES So(J=0-4) OF H_2: FREQUENCIES,
BROADENING AND SHIFTING COEFFICIENTSAS A FUNCTION
OF TEMPERATURE FOR DIFFERENT PERTURBERS

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In a first part, we present accurate measurements of $S_0(0)$ to $S_0(4)$ transitions of H_2 by Stimulated Raman Spectroscopy. Combined with Q branch frequencies, these data allow us to calculate rotational and rovibrational interstellar quadrupolar spectrum of H_2 for the first time with a very high accuracy.

In a second part, we discuss collisional effects in pure rotational spectra of H_2. We investigated broadening and shifting parameters between 300 and 1000 K at pressure up to 30 bars for pure H_2, H_2-He, H_2-N_2 and H_2-Ar mixtures.

The data are analysed to obtain information about the collisional processes; in particular, with respect to the speed dependence of parameters which are responsible for the asymmetry of the lineshape and for the non-linearity of line broadening versus perturber concentration in the Q branch [1, 2].

In the pure rotational branch, no asymmetry is observed although non-linearity persists for H_2-Ar [3] and H_2-N_2 mixtures. We analysed these two facts using the speed-dependent RTBT-$\gamma(v)$ model[2] which takes into account the competition between inhomogenous broadening due to speed-dependent shifting δ (v) and inhomogenous narrowing due to speed-dependent broadening γ (v).

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D18

THE POTENTIAL ENERGY SURFACE AND VIBRATIONAL-ROTATIONAL ENERGY LEVELS OF HYDROGEN PEROXIDE

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The six-dimensional potential energy surface of hydrogen peroxide, H_2O_2, has been determined from large-scale *ab initio* calculations using the coupled-cluster method, CCSD(T), with the basis set of quadruple-zeta quality, cc-pVQZ. The effect of core correlation on the calculated structural parameters and the torsional potential energy function has been investigated. The anharmonic quartic force field has been determined. The vibrational-rotational energy levels of the molecule have then been calculated using the variational method and are found to be in good agreement with experimental data.

CONCEPTION OF A MULTISPECTRUM NONLINEAR LEAST
SQUARES FITTING PROGRAM : APPLICATION TO CH4

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In our laboratory. least squares fit technique is usually applied individually to the spectra recorded at different pressures in order to derive the spectral parameters (wavenumber, line intensity and broadening coefficient) from rovibrational lines. In this case. the error bars determination is difficult as it may be distorted by the operator's intervention.

We have developed a multispectrum nonlinear least squares fitting technique (multifit technique) based on Carlotti's[1] and Benner et al. studies[2] to obtain more accurate spectral parameters (in particular line intensity and broadening coefficient). This procedure runs automatically by fitting all parameters.

It has been applied to laboratory spectra of CH_4 recorded at pressures taken between 8 and 200 torr, provided by the Kitt Peak National Observatory. The results from this study for lines in the spectral region near 1.1 µm are consistent with those obtained by means of individually fitted spectra but more accurate. Therefore the advantages of this method have been reached well with regard to accuracy of measurements and automatic treatment of spectra.
We present here the comparison of the results of both methods, showing the advantages of the multifit technique.

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D20

HYDROGEN CYANIDE: THEORY AND EXPERIMENT

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Results of large-scale ab initio calculations for hydrogen cyanide are compared with available experimental data. The equilibrium bond lengths of the electronic ground state are obtained with an accuracy of ca. 0.0005 Å and the wavenumbers of the fundamental vibrational transitions have errors of 2.1 cm^{-1} (ν_1), 1.3 cm^{-1} (ν_2) and 5.8 cm^{-1} (ν_3). An accurate three-dimensional CCSD(T) electric dipole moment is reported and, by combination of experiment and theory, the equilibrium dipole moment is obtained to be μ_e = -3.0146(5) D. The calculated transition dipole moments of the ν_3 bands of HCN isotopomers agree with experiment and the intensity anomaly found experimentally for $H^{12}C^{14}N$ and $H^{12}C^{15}N$ is reproduced by theory for the first time. Accurate equilibrium geometries are reported for the two lowest electronic states of HCN^+ ($X^2\Pi$ and $A^2\Sigma^+$). By combination of experimental and theoretical data, the equilibrium excitation energy of the first excited singlet state ($\tilde{A}^1A''$) is obtained to be T_e = 53 266 ± 30 cm^{-1}. The equilibrium geometry of the lowest triplet state ($\tilde{a}^3A'$) is r_e = 1.102 Å, R_e = 1.290 Å and α_e = 120.9 °. Its T_e value is recommended to be 38 500 ± 500 cm^{-1}.

D21

MOLECULAR BEAM STUDIES OF ScNH AND ScS

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Scandium's limited number of valence electrons and its low atomic number makes scandium containing molecules ideal for both experimental and theoretical investigations of bonding properties. The most insightful bonding information comes from an interpretation of hyperfine interactions and measurement of the permanent electric dipole moment, μ. Molecular beams of ScS and ScNH were generated by skimming the products of a laser ablation/reaction supersonic expansion source. The near natural line width spectra of the $A^2\Pi - X^2\Sigma$ band system of ScNH and the $B^2\Sigma - X^2\Sigma$ band system of ScS were recorded both field free and in the presence of a static electric field. This is the first identification of ScNH. A comparison of the determined magnetic hyperfine interaction parameters and dipole moments for the isoelectronic series ScO^1, ScS and ScNH is produced.

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D22

Rotational Analysis of Tantalum Oxide, TaO

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Doublet bands of TaO between 7000 and 28000 cm^{-1} have been recorded in emission with FTS techniques using an electrodless 2450 MHz discharge. Fifteen electronic states have been recorded and analysed , of which three states have not been reported earlier. The ground state (a regular $^2\Delta$ state) parameters have been improved since it was found that two states more then earlier observed have transitions to both subsystems of the ground state. In addition to these states two more states have been analysed due to a transition at 10025 cm^{-1}, none of these states have a transition to the either the ground state or to the fifteen exited states of this work. The transition has been assigned to a $^2\Pi_{1/2}-^2\Sigma_{1/2}$ transition. The Hund's case (c) behaviour of this molecule makes it difficult to be described by Hund's case (a), except for the ground state. One interesting feature in this work is a local perturbation in the N $^2\Delta_{3/2}$ state. The term value representation of the perturbation shows a derivative-like shape with normal (unperturbed) intensity variation around the centre of the perturbation. So far no progress has been achieved in describing this perturbation analytically. But hopefully this problem is solved before the conference.

Microwave spectrum and structural parameters of
methyl-cyclopentadienyl-manganese-tricarbonyl

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Transition metal carbonyls are of interest as catalysts for many industrial processes. In the U.S.A. Methyl-cyclopentadienyl-manganese-tricarbonyl $CH_3-Cp-Mn(CO)_3$ is used as a substitute of lead-tetraethyl in fuel.

Metal carbonyls show up a very interesting bonding situation and may be regarded as model systems for many chemical reactions.

The microwave spectrum of methyl-cyclopentadienyl-manganese-tricarbonyl has been recorded in the range from 1 to 23 GHz using molecular beam FT microwave spectrometers. The rotational spectrum was assigned and from the rotational constants some structural parameters of this molecule could be determined. The rotational lines revealed a hyperfine structure due to quadrupole coupling of the manganese nucleus and also a fine structure due to the internal rotation of the methyl group. This fine structure could be assigned, too, and the quadrupole coupling constants and the torsional barrier could be obtained. The spectrum is an a- and c-type spectrum according to the structural assumption based on the structure of related compounds.

Internal Rotation in the Microwave Spectrum of CH$_3$BCl$_2$: An Improved Analysis

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An earlier microwave investigation[1] has shown CH$_3$BCl$_2$ to have a low barrier to internal rotation of the methyl group. The familiar model[2] used in the analysis was found to be deficient for the excited torsional states of CH$_3$BCl$_2$ and CD$_3$BCl$_2$. Since then the model has been extended[3] by introducing geometry relaxation terms allowed within the G_{12} symmetry group, but disallowed for D_{6h} symmetry.

This extended model is now used to re-analyse the microwave spectrum of CH$_3$BCl$_2$, and it is demonstrated that these extra "symmetry breaking terms" are important in fitting the spectrum. Thus it has been possible to obtain a global fit of most of the measured lines with a standard deviation of 0.1 MHz. Some changes in assignments were required in a few cases, however.

The spectrum of the D$_3$ species has also been re-analysed, but further experimental work is desirable. Improved precalculations will allow this for both CH$_3$BCl$_2$ and CD$_3$BCl$_2$. An improved V_6 barrier and methyl group structure will be reported.

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MILLIMETER WAVE SPECTRUM

OF ACETIC ACID CH$_3$COOH.

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We report experimental study of the millimeter wave spectrum of acetic acid between 55-155 GHz. In our measurements we used millimeter wave spectrometer with frequency synthesizer that can provide accuracy of frequency measurements about 3kHz. At a first stage of our study we have performed a continuous recording of the spectrum in the 60-115 GHz frequency range and have obtained over 2700 transition frequencies of CH$_3$COOH. At the second stage in order to improve the fit some of these transitions have been remeasured more precisely along with measuring of the significant weak transitions which were not available via continuous recording mode of spectrometer. Obtained experimental data and those available from literature were treated with IAM effective torsion-rotational Hamiltonian. Fitting A and E transitions of the ground and excited torsion-rotational states we have obtained more accurate set of constants.

D26

Laser Photofragment Spectroscopy of GeH$^+$.

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High resolution (< 0.005 cm^{-1}) electronic spectra of the diatomic molecular ions ^{70}GeH$^+$ and ^{74}GeH$^+$ have been recorded using a fast ion beam irradiated by a cw tunable dye laser. Over 150 transitions between the ground X$^1\Sigma^+$ state and near threshold levels of electronic states correlating to the lowest dissociation asymptotes Ge$^+(^2P_{\frac{3}{2}})$ + H(^{2}S) and Ge$^+(^2P_{\frac{1}{2}})$ + H(^{2}S) were observed in the range 16500 cm^{-1} to 18500 cm^{-1}.

The majority of the lines arise from a $^1\Pi$-$^1\Sigma$ transition, where the predissociated excited state levels lie between the fine structure dissociation limits (Feshbach Resonances). The lifetimes of the rovibrational levels are found to increase with increasing rotational quantum number. Evidence for triplet (multichannel) mixing is revealed through the observation of additional lines and proton nuclear hyperfine splittings.

Experimental results are compared with predictions of the vibrational and rotational energy levels obtained from a numerical solution of the Schrödinger equation. Least squares fitting yields molecular constants for the $^1\Sigma$ and the $^1\Pi$ states.

VIBRONIC STATES OF NONRIGID MOLECULES AS AN OBJECT OF
A HIGH RESOLUTION SPECTRUM THEORY

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As a matter of fact the high resolution spectrum theory is that of rotational structure of molecular spectra. Its greatest success has been achieved by employing effective model hamiltonians, although the necessity of using ab initio constrained methods is realized.

In this report the rigorous nonrelativistic theory of rovibronic spectrum description on the basis of our latest variant of a rovibronic hamiltonian in the principal axes of inertia is considered. In this hamiltonian the operator of rotational kinetic energy is written in the classic form which possesses no unphysical singularities. The use of group methods enables one to rewrite the hamiltonian in such a form which determines completely the rotational structure of a spectrum and selects the vibronic part of the hamiltonian. This part allows one to determine both the ground and excited states of the nonrigid molecules. The expressions of all hamiltonians obtained are given. The ways of their use are discussed.

D28

SUBMILLIMETRE-WAVE KINETIC SPECTROSCOPY OF CH_3O
PRODUCED BY EXCIMER LASER PHOTOLYIS

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The methoxy radical is an important molecule in both fields of
combustion and atmospheric chemistry. Furthermore, it possesses a rare
molecular structure: it is a symmetric top with an orbitally degenerate ^2E
electronic ground state. Owing to its high reactivity the first zero-field rotational
spectrum of this molecule was only reported in 1984. In this previous work[1]
CH_3O was produced by a reaction involving fluorine atoms generated by
microwave discharge.

We are presently studying the submillimetre-wave spectrum of this
molecule produced by ultraviolet excimer laser excitation of CH_3ONO at 248 nm.
The pulsed laser radiation has allowed the use of kinetic spectroscopy to eliminate
the strong precursor spectrum. The radical is created after each laser pulse and is
subsequently eliminated by reaction. During a frequency scan the time-dependent
signal is recorded at each frequency point. The data is then treated so that only the
spectrum of a molecule of a particular lifetime is observed.

Our aim is to improve the molecular constants of this molecule by
measuring at much higher frequencies than in the previous study. Measurements
up to nearly 1 THz should be possible using recently acquired Russian-constructed
BWO tubes.

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Microwave Spectrum and Internal Motion of the Furan–CO Van der Waals Complex

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Several Van der Waals complexes between aromatic molecules and CO have been studied in recent years. Contrary to the corresponding rare gas complexes, the structures of these complexes show various geometries. In benzene and pyrrole, CO was found to be located above the ring plane while for pyridine an in-plane complex is favoured with the CO attached asymmetrically between nitrogen and the adjacent hydrogen. It is not obvious which configuration is more stable for the furan–CO complex.

The rotational spectrum of furan–CO has been measured with a pulsed jet Fourier transform microwave cavity spectrometer between 6–25 GHz; 107 pure rotational and 8 ro-torsional transitions have been identified. Most of the transitions are split into two equally intense components with splittings ranging from a few kHz to several MHz. Transitions sharing an energy level have been assigned using double resonance experiments.

Reducing the split transitions to their hypothetical line centres and fitting a rigid rotor Hamiltonian to them has led to rotational constants that are compatible only with CO located above the ring plane. The splittings have been explained by internal rotation of CO parallel to the ring plane between two equivalent positions. This model has been found to fit the observed spectrum to nearly experimental accuracy.

The Calculation of the Bound and Quasibound Vibrational States for Ozone in its $^1B_2$ Electronic State

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The bound and quasibound vibrational states of ozone in the $^1B_2$ electronic state have been calculated using the stabilization method. The calculation was based on an *ab initio* potential energy function from the literature. From the topology of this surface, we determine the molecular symmetry group of $^1B_2$ O_3 to be $C_{2v}(M)$. The parameters of resonances in the 750-2750 cm^{-1} energy range relative to the $O_2(^1\Delta_g)$ + $O(^1D)$ dissociation limit are given. The effective vibrational constants obtained by fitting the calculated vibrational energy levels are compared to the corresponding experimental values. The agreement is satisfactory and supports the assignment of the Huggins band to the $^1B_2 \leftarrow X\,^1A_1$ electronic transition.

D31

THE ELECTRIC DIPOLE MOMENT OF YTTERBIUM MONOXIDE

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Previous experimental spectroscopic data[1] on the ytterbium monoxide molecule, YbO, have indicated that the ground state is a $^1\Sigma^+$ state originating from the closed $4f^{14}$ of the Yb^{-2} ion. Ab initio calculations[2,3] disagree on the ordering of the low-lying states of the $4f^{13}6s$ superconfiguration relative to that of the $4f^{14}$ configuration. The $4f^{13}6s$ superconfiguration is expected to have the smaller dipole moment because of the large back-sided polarization of the 6s orbital. We therefore decided to try and measure the dipole moment in an attempt to resolve this issue and gain a better understanding of the configurational nature of the ground state.

A supersonic molecular beam of ytterbium monoxide, YbO, was produced by reacting Yb atoms with oxygen in a laser ablation source, passing the beam through a pair of Stark plates and applying an electric field. The beam was interrogated by a single mode ring dye laser tuned to the R(1) line of the A $\Omega = 0^+ - X\ ^1\Sigma^+$ transition at 579 nm., and from the Stark shifts of the lines, dipole moments of 5.931(43) and 5.888(16) Debye were determined for the upper and lower states respectively. The details of this investigation will be presented and the results discussed in terms of the electron configurations of the two states.

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RYDBERG STATES OF RARE GAS HYDRIDES

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The first observed spectra of rare gas hydrides were those of ArH
and ArD by Johns in 1970. Subsequently, spectra of RgH and RgD
with Rg = He, Kr and Xe have been observed and analysed, mainly
by groups in Garching and Ottawa, while bands of NeH and NeD have
been observed in Garching but are not understood at present. Progress
for ArH and ArD was slow because many of the observed bands go to
the low-lying $4p$ state, which is of almost pure Hund's case (d), and
the rotational structure was difficult to recognise. The rare-gas hydride
bands of interest here are all of Rydberg-Rydberg type, and the effective
electronic-rotational Hamiltonian and approximate energy levels will be
described, and the meaning of some of the parameters will be discussed.

E2

HIGH SENSITIVITY LASER SPECTROSCOPY OF MOLECULES AND IONS IN THE
NEAR INFRARED REGION

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Doppler–limited laser spectroscopy combined with sensitive detection schemes has been proven to be a suitable method for the identification and the study of molecular species characterized by small signals, either because the species are produced in weak concentration, or because of the intrinsic weakness of the observed transitions.

After a general introduction and a short review of the currently available techniques the talk will concentrate on two selected subjects studied in Lille, using a cw Ti:Sa laser : the rovibrational structure of stable molecules in highly excited states and the electronic transitions of molecular ions.

The experimental characterization of the structure of highly excited vibrational states of polyatomic molecules presents a fundamental interest for the development of models able to take into account the effects related to the anharmonicity of the potential energy surface. Overtone spectroscopy is a rather simple and efficient method, and the photoacoustic detection technique is appropriate to reach a good sensitivity. It will be illustrated by recent results obtained for the carbonyl sulfide molecule.

Because of their considerable astrophysical interest, the study of molecular ions is still today a challenge for theoreticians and experimentalists. Molecular ions are reactive species and must be produced in–situ, for example in electric discharges, and by means of chemical reactions. Only weak concentrations are obtained and often the optimum production conditions are unknown. Therefore spectroscopic studies require sensitive detection techniques. An additional difficulty is coming from the fact that a variety of species may be formed and gives rise to a complicated spectral pattern. Therefore a *selective* detection scheme, the velocity modulation technique, is used to record absorption spectra. Recent results related to H_2O^+, and to HDO^+ and $TiCl^+$ in the visible, will be presented.

F1

REMPI SPECTROSCOPY OF 2-METHYLPROPANAL

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The (n,3s) Rydberg spectra of 2-methylpropanal (isobutyraldehyde) and its mono-deuterated derivative have been studied employing one-colour (2+1) REMPI spectroscopy with a pulsed tunable dye laser and supersonic jet-cooling with parallel plate detection of the photoion current. Two separate, well-defined electronic origins have been located in the region around 54 000 cm^{-1} for the prevailing *gauche* conformers and the less stable s-*trans* conformer implying a four-fold increase to 1064 cm^{-1} in the energy difference between the two conformers in the excited state. The spectra show prominent progressions in skeletal bending and torsional motions of the excited state. The vibrational analysis of the spectra and potential functions for the asymmetric torsion of the aldehyde group in the (n,3s) Rydberg will be reported.

F2

FREE JET ABSORPTION MILLIMETER WAVE SPECTROSCOPY OF SATURATED 7-MEMBERED RINGS: 1,3-DIOXEPANE

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The free jet millimeter wave spectrum of dioxepane has been investigated in the 60-78 GHz region. The spectrum corresponds a rigid C2-symmetry asymmetric top. The effects of the hypothetical "pseudorotation" are not as important as suggested in previous investigations.

F3

HIGH-RESOLUTION ABSORPTION SPECTROSCOPY OF OZONE AND ITS ISOTOPOMERS IN THE NEAR-INFRARED

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High resolution absorption spectra of the 1-0 symmetric vibration v_2 of the $^3A_2$ state have been recorded with an external cavity tunable diode laser spectrometer for symmetric and asymmetric ozone isotopomers formed by combinations of ^{16}O and ^{18}O ($^{16}O^{16}O^{16}O$, $^{16}O^{18}O^{16}O$, $^{16}O^{16}O^{18}O$, $^{18}O^{18}O^{16}O$, $^{18}O^{16}O^{18}O$, $^{18}O^{18}O^{18}O$). Spectra of mixed isotopomers have been observed for the first time. The assignment of the rotational bands has been performed with combination differences using spectroscopic constants of the ground state. All isotopomers were clearly identified. Some rotational lines are completely resolved yielding line profiles and line widths. The line widths yield upper limits for the lifetime of the electronic state which are in the range of 50 - 100 ps without any systematic differences for different isotopomers. The observed symmetric vibration v_2 is dissociative for all isotopomers probably due to a strong coriolis coupling to the asymmetric vibration v_3. The spectroscopy will be extended to investigate the 0-0 symmetric vibration v_2 and a comparative study will be presented.

A characterization of these vibrational bands allows to assess the relevance of these states to the ozone production in the Chapman reaction, particularely *the heavy ozone problem*.

115

N_2-, O_2-, AND AIR-BROADENING COEFFICIENTS OF THE J=3 ← 2 LINE OF CO AND THE J=$34_{2,32}$ ← $34_{1,33}$ LINE OF O_3,

MEASURED WITH TWO TECHNIQUES: TUNABLE MICROWAVE SOURCE AND FOURIER-TRANSFORM SPECTROSCOPY.

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Experiments were performed with both, i) a tunable microwave source spectrometer operated in video mode and ii) a commercial high resolution Bruker IFS 120 HR Fourier-Transform spectrometer.

i) Pure rotational transitions of CO and O_3 have been studied at 3 temperatures (range 247-296K) with N_2 and O_2 as broadening gases(pressure of the perturber from 0 to 400 mTorr). Analyses of the experimental absorption signals were made using Voigt lineshape functions. Air broadening parameters γ (air) are retrieved from N_2 and O_2 results, using the usual relation: γ (air)=0.79 γ (N_2)+ 0.21 γ (O_2)

ii) Since the FT spectroscopy is less sensitive, some basic considerations concerning precision of FT-determination of pressure broadening parameters are presented.

Pure rotational transitions of CO and O_3 have been studied in the spectral range 11-28 cm^{-1} , which is quite unusual for commercial FT spectrometers. The temperature ranged from 190 to 300K, the broadening gas pressure was between 40 and 80 mb. In case of CO lines up to J"=6 have been measured. In an attempt to enhance the precision for the target line (J"=2), the pressure broadening parameter and the temperature exponent have been expanded as polynomial in J.

The results obtained with different spectroscopic techniques will be compared and discussed as well as the results of an analysis of combined data.

A study of the halogen oxides by infrared and far-infrared laser magnetic resonance.

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The 2-0 overtone bands of the FO and BrO radicals in their $X^2\Pi_{3/2}$ electronic ground states have been studied by CO laser magnetic resonance. Attempts have also been made to detect the fine-structure transition $^2\Pi_{1/2} \leftarrow ^2\Pi_{3/2}$ of FO by FIR LMR around 200 cm^{-1}; some tentative assignments have been made.

Least-squares fits of all available data allowed the determination of a number of virational, rotational, centrifugal distortion, spin-orbit, hyperfine, lambda-doubling and Zeeman parameters for both molecules.

Moreover, the analysis provides the first experimental measurement of the anharmonicity constant $\omega_e x_e$ for BrO:

$$^{79}\text{BrO} \quad \omega_e x_e = 4.675\ 83(43)\ \text{cm}^{-1}$$
$$^{81}\text{BrO} \quad \omega_e x_e = 4.657\ 03(39)\ \text{cm}^{-1}$$

DIRECT ℓ -TYPE RESONANCE AND ROTATIONAL SPECTRA OF PF$_3$ IN THE VIBRATIONAL STATE $v_4=1$

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In 1994, we started to apply the concept of fitting transition frequencies of symmetric top molecules with C_{3v} symmetry in isolated excited degenerate states using unitary equivalent sets of parameters[1]. This concept of 'multiple fitting' has been extended and revised in following papers[2,3]. PF$_3$ is an interesting molecule for the application of this concept due to very strong direct ℓ-type resonance spectra in the vibrational state $v_4=1$ covering large ranges of the quantum numbers J and $|k-\ell|$. The observation of direct ℓ-type resonance transitions by means of Stark spectroscopy has already been reported by Hirota[4] in 1970 allowing the determination of several rotation-vibration parameters. Measurements in Kiel by means of microwave Fourier transform spectroscopy have significantly extended the range of J and $|k-\ell|$ up to 60, while improving the accuracy of the data by a factor of 100 to 1000. These data have been combined with rotational spectra following the selection rule $\Delta J=1$, $\Delta k=0$, which have been observed in Lille using millimeter and sub-millimeter spectroscopy. The analysis of these data using two reduction schemes yielded highly precise parameters which perfectly fulfill relations following from the theory of reduction and which will be useful in calculating the anharmonic force field.

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F7

LINE-BROADENING STUDIES OF DIRECT ℓ -TYPE RESONANCE TRANSITIONS OF PF$_3$ IN THE VIBRATIONAL STATE $v_4=1$

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Broadening and shifting of molecular rotational lines is conventionally studied by analysis of absorption line shapes obtained by frequency-domain measuring techniques. These techniques were supplemented in recent years by time-domain techniques which employ the observation of a coherent transient emission signal after pulsed excitation of the molecules in order to create a macroscopic polarization of the sample. This is achieved by methods to switch either the microwave power or frequency, or the energy level difference (Stark-switching).

We have applied in our experiments the power switching technique[1] which has mostly been used so far in the centimeter-wavelength region and which is particularly suitable for lineshape studies of weakly-allowed transitions. As far as symmetric top molecules are concerned, experiments in this frequency range are commonly performed on R-branch rotational transitions, covering only a small range of quantum numbers J and k. Thus, it was particularly interesting to investigate the broadening and shifting of ℓ-type resonance lines of PF$_3$ in the vibrational state $v_4=1$ which cover a much larger range of quantum numbers J and $|k\text{-}\ell|$ (up to 60). Results on the dependence of line self-broadening and -shifting data on these quantum numbers will be reported and discussed.

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NEW HIGH RESOLUTION ANALYSIS OF THE v_3, v_4, and v_6 BANDS
OF D$_2$CO MEASURED BY FOURIER TRANSFORM SPECTROSCOPY

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A reanalysis of the v_3, v_4, and v_6 bands of D$_2$CO has been carried out in
the 900-1200cm^{-1} region using high resolution Fourier transform spectra
recorded at Giessen. As compared to the previous study of these bands,[1]
improvements were obtained in the present analysis. In order to get the
upper state parameters (band centers, rotational and coupling constants), the
resulting v_3=1, v_4=1, and v_6=1 experimental energy levels were introduced
in a least squares fit calculation together with the microwave measurements
available in the literature. In this calculation, which made it possible to
reproduce both the infrared and microwave measurements within their
experimental accuracies, the A- B- and C- Coriolis type interactions
involving the v_4=1 and v_6=1, v_3=1 and v_4=1, and v_3=1 and v_6=1 energy
levels respectively were explicitly taken into account. Also, from the
intensities, a new determination of the relative values of the q_3, q_4, and q_6
first derivatives of the D$_2$O dipole moment was performed.

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Emission Spectrum of HCN at 1400 K in the Region of the Bending Fundamental

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The emission spectrum of HCN heated to 1400 K has been measured[1] in the region from 500 to 850 cm^{-1} with a resolution of 0.005 cm^{-1}. All of the states in the bending manifold for HCN have been measured through the $09^9 0$ state with the exception of the $09^3 0$ state. In addition we have measured the $010^{10} 0$-$09^9 0$ R-branch transitions.

The $\Delta v_2 = 1$ transitions were also observed for all the levels of the type $0N^n 1$ through $05^5 1$. Again the strongest of the next higher set of transitions were measured, the R-branch of $06^6 1$-$05^5 1$.

Although quantitative measurements have not been made, the relative intensities are in approximate agreement with the expressions given in our earlier paper[2]. The constants given by the analysis of the present measurements are in excellent agreement with our earlier[3] predicted values for the $07^n 0$ and $05^n 1$ states, the vibrational term values agreeing within .0.022 cm^{-1}.

The present analysis greatly improves the accuracy of the centrifugal distortion constants D_v and H_v beyond previous measurements because transitions of higher rotational levels were measured, including levels up to $J = 65$ for the ground state and the first bending state. Improved values have been determined for the vibrational power series expansion of the various rovibrational constants. These constants can be used to accurately predict all the energy levels below 8000 cm^{-1}.

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STRONG AND ISOTOPE SELECTIVE EFFECTS OF THE $\Delta K = \pm 3$
INTERACTION IN THE GROUND STATE AND IN THE ν_5 INFRARED
BANDS OF FOUR ISOTOPOMERS OF $FC\ell O_3$

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The infrared spectra of monoisotopic samples of the $^{35/37}C\ell$ and $^{16/18}O$ isotopomers of $FC\ell O_3$ have been recorded in the region of the ν_5 fundamental with a resolution of ca. 3×10^{-3} cm^{-1}. Several thousand lines have been assigned in each species and ground state molecular parameters have been determined or improved through the use of Ground State Combination Differences. It was shown that an agreement between the ground state parameters of the four isotopomers requires a $\Delta K=\pm 3$ interaction with an off-diagonal ε term introduced. This is clearly due to the fact that these molecules, especially with ^{18}O are quasi-spherical tops.

The main perturbation in the $\nu_5=1$ state is due to a $\Delta K=\pm 3$ interaction which has very strong effects because levels differing by 3 units in K can be unusually close. For $F^{35}C\ell^{18}O_3$ and $F^{37}C\ell^{18}O_3$, the effects are largest for $k\ell=-23$ and -26 and give rise to 'perturbation-allowed transitions'. For $F^{35}C\ell^{16}O_3$ and $F^{37}C\ell^{16}O_3$, the $k\ell=-5$ and -8 levels are closest and no perturbation-allowed transition could be assigned. Two different interaction terms, called ε and d, can be defined for such interactions in a degenerate vibrational state. For the first time, they have been both determined significantly and simultaneously for all four isotopomers. They adopt values almost independent of $^{35}C\ell/^{37}C\ell$ substitution and consistent in the $^{16}O/^{18}O$ substitution, in spite of very different resonance effects. The axial rotational constants A_0 have also been determined with high accuracy.

F11

CAN ISOTOPIC SUBSTITUTION CHANGE A BRIGHT STATE INTO A DARK STATE? THE CASE OF THE $V_3=1$ STATE OF $FC\ell O_3$

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High resolution infrared spectra of monoisotopic samples of $F^{35}C\ell^{18}O_3$ and $F^{37}C\ell^{18}O_3$ have been recorded with the purpose of analysing the v_3 fundamental at 535 cm^{-1}. However this band could not be observed whereas it had been seen and studied earlier in $F^{35}C\ell^{16}O_3$. In order to determine the parameters of the $v_3=1$ state, indirect methods were used. Hot bands $v_n + v_3 - v_3$ (n=1 or 2) were first analysed and their LSCD (Lower State Combination Differences) yielded rotational parameters of v_3. Then, with the help of $v_1 + v_3$. all rovibrational parameters of v_3 were obtained.

Similar methods were applied to spectra of $F^{35}C\ell^{16}O_3$ and $F^{37}C\ell^{16}O_3$ to prove that the parameters of v_3 obtained in this fashion are identical to those determined directly for these isotopomers and even more comprehensive.

It is shown that the different character of v_3 in the two ^{18}O and in the two ^{16}O isotopomers is due to the fact that the former are much closer to a spherical top molecule ($(A_0 - B_0)/ A_0 = 0.015$). This is not only reflected in intensities different by orders of magnitude but also in the very different values of α_3^B in these two pairs.

HIGH-RESOLUTION SPECTROSCOPY OF THE ν_3 BAND OF WF$_6$ IN A SUPERSONIC JET

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We have recorded the Fourier-transform spectrum of the ν_3 fundamental band of WF$_6$ in a continuous supersonic expansion jet with an instrumental bandwidth of 0.0024 cm^{-1} (FWHM, unapodized), using a Bomem DA.002 spectrometer [1]. Some parts of this band have also been recorded with 0.0007 cm^{-1} bandwidth using a laser-diode and a pulsed slit jet [2]. A multiple-pass set-up has been used to observe low-intensity lines. In each case, we have used a WF$_6$:He mixing with a seeding ratio 1:4 leading to a rotational temperature of ca. 50 K.

This work extends upon the investigation of Takami and Kuze [3], since we have observed higher J values. In both P and R branches, rotational lines have been recorded for J up to 46–48.

Refined parameter values are given. We have used a tensorial hamiltonian adapted to the group chain $O(3) \supset O_h$ and developed to the third order. A least-squares fit has then been performed for each of the four isotopic species : ^{182}WF$_6$, ^{183}WF$_6$, ^{184}WF$_6$ and ^{186}WF$_6$.

We will also report most recent results on ReF$_6$.

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OZONE : ANALYSIS OF $v_1+2v_2+3v_3$ AND $4v_1+ v_3$ BANDS. LINE POSITIONS AND INTENSITIES.

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The very weak bands $v_1+ 2v_2+ 3v_3$ and $4v_1 + v_3$ of $^{16}O_3$ have been observed for the first time, using the Fourier Transformed Spectrometer (FTS) of Reims and the usual experimental set-up providing a large product $p \times \ell$: approximately 38 Torr x 36 m. The upper levels of these A type bands which are rather close (they appear respectively at 5291.722 and 5307.790 cm^{-1}) belong to two different sets of interacting polyads. To correctly reproduce the rotation-vibration energy levels taking into account the observed perturbations, both bands are treated in a dyad approximation : the (123) state in the Coriolis resonance with the (330) state, and the (401) state in the Coriolis resonance with the (024) state. The assignment of (123) state rotation-vibration levels is confirmed by measurements of line positions of the hot band $v_1+ 2v_2+ 3v_3- v_2$ which has also been observed for the first time. The fits are very satisfactory : the r.m.s. deviation for 249 energy levels of the (123) state is 2.4×10^{-3} cm^{-1} and is 2.0×10^{-3} cm^{-1} for 266 levels of the (401) state. These r.m.s. are near the experimental accuracy. Transition moments for the three observed bands are determined from measured line intensities.

Information System for Modeling High Resolution Spectra of Polyatomic Molecules

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The new MIRS4 project is concerned with high resolution spectroscopy of symmetric polyatomic molecules. It uses new computational algorithms for the modeling of complex interacting band systems (so-called polyads). MIRS4 works with an arbitrary number of interacting vibrational modes and with arbitrarily high vibrational polyads. The programs have already been tested for the C_{3v}, T_d and O_h groups. The purpose of MIRS4 is the construction of operator series with unknown parameters for the interpolation and the approximation of energy levels and transition intensities of polyatomic molecules. Such series represent effective Hamiltonian and dipole moment operators. The application field of MIRS4 is wider than that of TDS [1] or STDS [2]. A friendly interface for Windows 95 version of MIRS4 is realised as a full MDI server [3] with full OLE2 support.

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THE POTENTIAL ENERGY SURFACE AND VIBRATIONAL-ROTATIONAL ENERGY LEVELS OF HOCL

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The potential energy surface of hypochlorous acid, HOCl, has been determined from large-scale *ab initio* calculations using the coupled-cluster method, CCSD(T), with basis sets of quadruple- and quintuple-zeta quality. The vibrational-rotational energy levels of the HOCl molecule have then been calculated using the variational method, and have been further characterized by the spectroscopic constants determined using the perturbational approach. The effects of the one-particle basis set and of core correlation on the calculated molecular parameters have been investigated. The spectroscopic constants determined at the most advanced level of theory used here are found to be in excellent agreement with experimental data.

THE APPLICATION OF A VUV-FT SPECTROMETER AND SYNCHROTRON RADIATION SOURCE TO MEASUREMENTS OF THE O_2 AND NO BANDS

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The Imperial College VUV-FT spectrometer has been equipped with optically contacted, beam splitters made from single crystals of MgF_2 and the short wavelength performance has been demonstrated down to ~139 nm. To make ultrahigh resolution VUV photoabsorption cross section measurements with the VUV-FTS require a pure continuum source below 190 nm and the best choice is synchrotron radiation from a storage ring facility. Moreover a suitable zero-dispersion predisperser is available on beam line 12-B of the synchrotron radiation source at the Photon Factory. We therefore moved the IC VUV FT spectrometer from Imperial College, London to the Photon Factory, Japan to exploit the bandwidth-limited synchrotron radiation as a background source for FT absorption spectroscopy. We will present some preliminary results of O_2 and NO measurements.

A THEORETICAL INVESTIGATION OF THE ISOCYANIDES H₃CCCNC, NC₃NC AND HC₄NC

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$CCSD(T)$[1] calculations with the cc-pVTZ basis set[2] have been carried out for CH_3CCNC, NC_3NC and HC_4NC. Taking systematic errors of these calculations into account equilibrium bond lengths are predicted with an accuracy of better than 0.001 Å. The B_e values for NC_3NC and HC_4NC are 1408.7 and 1399.7 MHz and thus in excellent agreement with our previous predictions from less extensive calculations.[3] The corresponding B_0 values are expected to be slightly larger. Rather accurate values are predicted for a variety of spectroscopic properties like vibrational frequencies, vibration-rotation coupling constants, l-type doubling constants and transition moments.

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CALCULATION OF LEVEL LIFETIMES AND FRANCK-CONDON FACTORS FOR THE $B(^2\Sigma^-)$ - $X(^2\Pi)$ ELECTRONIC TRANSITION OF THE METHYLIDYNE (CH) RADICAL

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In this contribution theoretical calculations are reported for the ro-vibronic transitions between the B and X electronic states of the CH radical. Via the exact solution of the radial Schroedinger equation, using potential functions for the lower and upper states obtained from high-level multi-reference 'ab initio' methods, lifetimes are calculated for the v=1 rotational state in B. Some of these involve strongly predissociated levels. In addition Franck-Condon factors are also calculated for the band in question. Previous experimental studies shall be referred to in this connection [1,2].

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STRETCH-BENDER CALCULATIONS OF THE EFFECTS OF ORBITAL ANGULAR MOMENTUM AND VIBRATIONAL RESONANCES IN THE SPECTRUM OF SINGLET METHYLENE

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The stretch bender Hamiltonian for a symmetric triatomic molecule, which we have recently derived for a symmetric triatomic molecule (G. Duxbury, B. D. McDonald, M. van Gogh, A. Alijah and Ch. Jungen, Paper 1), has been used in conjunction with the Barrow, Dixon and Duxbury (Mol. Phys. **27**, 1217 [1974]) and the Jungen and Merer (Mol. Phys. **40**, 25-94 [1980]) methods of solving the Renner-Teller coupling problem in molecules which are executing large amplitude nuclear motion, to calculate the vibronic structure of the $\tilde{a}\,^1A_1$ and $\tilde{b}\,^1B_1$ states of the methylene radical CH_2. The results of the compact stretch-bender variational calculations are compared with the more extensive calculations of Green *et al.* (J. Chem. Phys. **94**, 118-132 [1991]) to show that good agreement between the two methods has been demonstrated. We have also compared the relative and complementary uses following the variation of the calculated expectation value of the orbital angular momentum, $<Lz>$, and of the "end over end" rotation constants B and q, as increasingly complex vibronic mixing is caused by the interplay between Renner-Teller and anharmonic coupling. In the present example the anharmonic coupling is principally due to Fermi resonance terms.

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THE EFFECTS OF VIBRATIONAL RESONANCES ON RENNER-TELLER COUPLING IN TRIATOMIC MOLECULES: THE STRETCH-BENDER APPROACH

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A vibration-rotation Hamiltonian for a symmetric triatomic molecule, based upon a stretch-bender reference frame has been derived. This frame is chosen so that as the molecule bends the reference geometry follows the minimum in the potential energy surface, thus minimising the size of the displacements required to reach the instantaneous axis geometry. This may be regarded as an extension of methods based upon the rigid bender reference frame approach developed by Hougen, Bunker and Johns (J. Mol. Spectrosc. 34, 136-172 [1970]).

This new stretch-bender Hamiltonian is combined with the Barrow, Dixon and Duxbury (Mol. Phys. 27, 1217 [1974]) and the Jungen and Merer (Mol. Phys. 40, 25-94 [1980]) methods of solving the Renner-Teller coupling problem in which molecules execute large amplitude nuclear motion, producing a compact method for the variational calculation of the energies of such a system. The $\tilde{a}\,^1A_1$ and $\tilde{b}\,^1B_1$ states of the methylene radical, CH_2, are used to demonstrate the use of this method for the analysis of the behaviour of strongly coupled electronic and vibrational states.

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Perturbation and Predissociation
in the $C\ ^1\Pi_u$ State of Cs$_2$

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The Cs$_2$ molecule is known to weakly predissociate in the lower vibrational levels of the $C\ ^1\Pi_u$ state. We have observed high-resolution spectra for the higher vibrational levels using the technique of Doppler-free optical-optical double resonance polarization spectroscopy (DFOODRPS). We found remarkable energy shifts and broadening in the rotational lines for $v \geq 13$. It indicates strong perturbation and predissociation in this energy region.

The break off of this predissociation at $v = 13$ is due to potential crossing with the repulsive $c\ ^3\Sigma_u^+$ state which correlates with Cs($^2P_{3/2}$) + Cs($^2S_{1/2}$). However, the vibrational and rotational dependence of the predissociation rate was rather complicated. In order to explain it, we considered the interaction with the $^3\Pi_u$ state which is a bound state located lower than the $C\ ^1\Pi_u$ state. We also observed and analyzed the spectra of the $^3\Pi_u$ state and determined the potential curve. The predissociation in the $C\ ^1\Pi_u$ state of Cs$_2$ can be understood by the interactions among these three electronic states.

F22

ROTATIONAL SPECTRA OF THE CYCLOBUTANONE···HCl AND
CYCLOBUTANONE···HF COMPLEXES

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The rotational spectra of the hydrogen bonded complexes cyclobutanone···HCl and cyclobutanone···HF have been studied in the frequency range 6-18.5 GHz using a molecular beam Fourier transform microwave spectroscopy.

For the cyclobutanone···HCl complex we have assigned the ground vibrational state of three different isotopomers ($C_4H_6O···H^{35}Cl$, $C_4H_6O···H^{37}Cl$, $C_4H_6O···D^{35}Cl$), for which we determined the rotational and quartic centrifugal distortion constants and the Cl-nuclear quadrupole coupling parameters. This hydrogen bond complex has been found to be planar. Structural information concerning the relative position of the HCl subunit has been derived from the quadrupole coupling constants. The geometrical properties of the hydrogen bond have been found to be: $r(O···H)=1.899(5)$Å, $<COH=111.59(17)°$ with a deviation of the hydrogen bond from linearity of 12.8°. An estimation of the stretching force of the dimer has been obtained from the centrifugal distortion constants.

For cyclobutanone···HF the assignement of the rotational spectrum of the ground vibrational state has been completed and further investigation is in progress.

THE STRUCTURE OF CARBODIIMIDE

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and

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Carbodiimide, HNCNH, is an accidently nearly symmetric top molecule [$\kappa = -0.999\,995\,383\,(12)$] with C_2-symmetry which undergoes internal rotation. The cis and trans energy barriers are of nearly equal height, about $2070\,\mathrm{cm}^{-1}$. An experimentally determined structure of HNCNH has not been reported so far. A chemical equilibrium exists between HNCNH and the more stable isomer cyanamide, H_2NCN, which strongly favors cyanamide (approximately 1:115 at 110° C). In this study we recorded rotational-torsional spectra of $HN^{13}CNH$ and $H^{15}NC^{15}NH$ obtained using isotopically enriched cyanamide in the millimeter wave region, and the rotational-torsional spectrum of DNCND in the far infrared region between 10-$350\,\mathrm{cm}^{-1}$. Rotational constants of the three isotopomers as for the parent species were calculated by fitting the assigned transitions to the Watson Hamiltonian in S-reduction. Using these rotational constants and fitting programs written by Schwendeman and Rudolph, r_0 and r_s structures of HNCNH were derived. The structural parameters will be compared with the *ab-initio* r_e structure obtained from a CCSD(T) calculation using Dunning's basis sets cc-pVXZ.

F24

SPATIAL MAPPING OF COLLISIONALLY COOLED GAS MOLECULES IN A COLD CELL

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We used a collisional cooling cell which was designed to mount directly on the second stage of a CTI-cryogenics Model 22C CRYODYNE CRYOCOOLER. The cell was maintained at approximately 14 K for all measurements reported. The absorption path length in the cell was 3.4 cm, and the window clear aperture was 1.27 cm. The injector was designed to be adjustable, so we could probe the cold gas cloud from the exit plane of the injector to approximately 11 millimeters downstream from the injector. We also could probe the cloud in a direction orthogonal to the previous direction. Our beam is imaged to a spot diameter of approximately 1 millimeter in the center of the cell.

Gas temperatures as low as 24 K were measured approximately 11 millimeters from the nozzle, and temperatures of approximately 40 K were measured close to the plane of the nozzle. Carbon monoxide was used as the analyte gas for all measurements. Absorbance values for the $R(1)$ line varied between 0.27 and 0.52 units ($-\ln T$) and for the $R(4)$ line the lowest absorbance values we used were 0.02 units. Rotational temperatures were in agreement with Doppler determined temperatures.

We are in the process of constructing a new cell with approximately 0.5 meter absorption path and eight injectors in an attempt to explore the possibility of improving the sensitivity of this technique. In the new cell we will be able to pass the beam more than one centimeter from the exit plane of the nozzles.

F25

INTRACAVITY LASER SPECTROSCOPY OF CO_2 TRANSITIONS
FROM EXCITED STATES

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Intracavity Nd-glass laser (ICL) spectrometer was used to study highly excited CO_2-states. The (20032)-(00001) transition of CO_2 (v_0=9517cm^{-1}) is situated near the high frequency end of Nd-glass laser generation. Unharmonicity of vibration leads to shift to the center of the Nd-glass laser generation, that allowes one to study CO_2 transitions with $\Delta V_1 = 2$, $\Delta V_2 = 0$, $\Delta V_3 = 3$ starting from the excited states.

The CO_2 spectrum has been recorded using the spectrometer at temperature 300...1350 K. Redistribution of the population in the range of high J-rotational quantum numbers allowed us to record (20032)-(00001) band up to J=88 and (21132)-(01101) band up to J=70.

Structure of the vibrationally excited CO_2 molecules was studed also in the CO_2-N_2 dicharge using ICL-spectrometer. CO_2 discharge of 60 cm long was placed inside the cavity Nd-glass laser with nondispersive resonator.

Spectrum of CO_2 discharge differs strongly from high temperature CO_2 spectrum. The transitions (21132)-(01101), (22232)-(02202), (30032)-(10001), and (20042)-(00011) were assigned in the spectrum and spectroscopic parameters of highly excited CO_2 states were determined.

F26

AN ELECTRON IMPACT SLIT JET IONIZATION SOURCE
FOR HIGH RESOLUTION SPECTROSCOPY
ON RADICALS, IONS AND IONIC COMPLEXES

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Slit jet expansions are routinely used for direct absorption spectroscopy of weakly bound molecular complexes, consisting from neutral species. In the last years attempts have been undertaken via plasma formation to extend this method to ionic complexes. Here we present a supersonic plasma technique based upon electron impact ionization. On the example of rotationally resolved spectra of N_4^+ [1] the characteristics of the set-up will be discussed. From mass spectra that have been recorded simultaneously, it is concluded that N_4^+ may play an important role as infrared probe for molecular nitrogen in environments such as planetary atmospheres [2]. Furthermore, it will be shown that this set-up is suitable for the detection of high resolution direct absorption spectra of ionic complexes.

[1] T. Ruchti *et al*, J. Chem. Phys., 105 (1996) 2591

[2] H. Linnartz *et al*, A&A, submitted

F27

Rotationally Resolved UV-Spectroscopy of Polyatomic Molecules: DFWM[1] of Benzene and REMPI[2] of Hydrogen-Bonded Clusters

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Rotationally resolved DFWM[1] spectroscopy of benzene in the bulk and REMPI[2] spectroscopy of hydrogen bonded clusters in a cooled molecular beam was performed with narrow band Fourier transform limited UV light pulses.

The room temperature spectrum of the $6_0^1 1_0^1$, $S_1 \leftarrow S_0$ electronic one-photon transition of gaseous benzene was measured using DFWM spectroscopy in "forward box" and "backward box" geometry. The rotational features can be fit to a symmetric top model using assigned transitions up to $J'=50$.

The intermolecular dynamics of phenol-water and the cluster structures of benzonitrile-water and benzonitrile-argon are investigated using the REMPI technique. A new correlation automated rotational fitting (CARF) procedure is presented for analyzing the complex rotational structure of the vibronic band. The highly resolved intermolecular vibrations of phenol-water are classified by the symmetry of the torsional state and the rotational constants. In the case of benzonitrile-Ar the position of the Ar is above the benzonitrile ring slightly displaced towards the C-N group, while in the benzonitrile-water cluster the water is found with its oxygen nearly in the plane of benzonitrile, nested between the cyano group and the ortho hydrogen.

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[1] DFWM: degenerate four-wave mixing
[2] REMPI: resonance enhanced multi photon ionization

Quantum beat spectroscopy of jet-cooled radicals: further results

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Quantum beat spectroscopy is a Doppler free method which has been used extensively for high resolution investigation of the spectroscopy and intramolecular dynamics of stable molecular species. By using either a pyrolysis or discharge nozzle, we have recently extended this technique to the study of jet-cooled transient species[1]. Radicals studied so far include OD, Ar · OD and NO_3. In this poster, we present further progress in this work, in particular an investigation of the $\tilde{B}$ state of the vinoxy radical C_2H_3O, produced from t-butyl vinoxy ether with electrical discharge. We have recorded the frequency domain spectra of the $(100) - (000)$ and $(010) - (000)$ vibrational bands of the $\tilde{B} - \tilde{X}$ transition at ~ 400 MHz resolution, resulting in a substantial improvement of the molecular constants for the upper state. We have also carried out quantum beat measurements on the nuclear hyperfine structure of the $\tilde{B}$ state. The analysis, which is complicated due to the three protons, is still in progress, but promises to yield very detailed information on the electron density distribution in the $\tilde{B}$ state. In addition, new work[2] has shown that the radical undergoes photochemical decay even at energies where fluorescence is observed. Analysis of our measurements should give insight into the nature and mechanism of this photochemical decay.

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K-Window Spectrum of Water in Sunspots

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Infrared absorption spectra of water recorded in sunspots by Wallace and Livingston [1] are analysed in the $4600 - 5100 \ cm^{-1}$ region where the water transitions are densest. Assignments which extend our analysis of pure rotational transitions of hot water [2] are made using variational nuclear motion calculations based on a high level *ab initio* electronic surface and with allowance for both adiabatic and non-adiabatic corrections to the Born-Oppenheimer approximations. 487 new transitions are assigned to transitions in 10 vibrational bands. Only two of these vibrational bands have been observed before in either the laboratory or space. Newly assigned bands include the $(061) - (050)$ and $(071) - (060)$ systems where even the lower energy levels have not previously been characterised.

[1] Wallace, L., & Livingston, W. 1992, An Atlas of a Dark Sunspot Umbral Spectrum from 1970 to 8640 cm^{-1} (1.16 to 5.1 μm) (NSO: Tech. Rep. 92-001)

[2] O.L. Polyansky, N. F. Zobov, S. Viti, J. Tennyson, P.F.Bernath and L.Wallace, Science, *in press*

PRECISE LABORATORY OBSERVATION OF THE
$^3P_2 \leftarrow^3 P_1$ TRANSITIONS OF ^{12}C AND ^{13}C

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We have precisely measured the transitions $^3P_2 \leftarrow^3 P_1$ of atomic carbon ^{12}C and ^{13}C with the Cologne terahertz spectrometer at 809 GHz. The transitions are observed by direct microwave spectroscopy, which results in improved accuracies ($\leq$400 kHz) in comparison with those achieved by the laser magnetic resonance (LMR)[1]. We applied a Zeeman modulation technique for the signal detection. Neutral carbon was produced by discharging a mixture of He and CO in a liquid nitrogen cooled discharge cell. The obtained rest frequencies for the $^3P_2 \leftarrow^3 P_1$ transitions are:

^{12}C: 809341.97(5) MHz

^{13}C:

$F = \frac{3}{2} \leftarrow \frac{1}{2}$: 809125.5(4) MHz
$F = \frac{5}{2} \leftarrow \frac{3}{2}$: 809493.7(2) MHz

Since these measurements were made the $F = \frac{5}{2} \leftarrow \frac{3}{2}$ transition of ^{13}C has been detected in interstellar space. Details of the spectrometer and its sensitivity limits will be discussed.

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[1] Cooksy et al. 1986

LABORATORY STUDY OF MONODEUTERATED METHANE SEEN IN THE PLANETARY WINDOW NEAR 6425 cm⁻¹

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The $3\nu_2$ band of CH_3D has been used to measure the D/H ratio in the atmospheric methane of Saturn, Uranus, Neptune[1] and the Saturnian satellite Titan. Measurements of the D/H ratio in CH_4, derived from the CH_3D/CH_4 ratio, provides information on interior models, on the origin of proto-planetary ices in the giant planets, and on the origin of the atmosphere of Titan[2]. Yet, the astrophysical constraints that measurements of the $3\nu_2$ band of CH_3D at 6425 cm⁻¹ could provide in these areas have been limited by the quality of the available planetary data and lack of detailed spectroscopic parameters, particulary line intensities and broadening coefficients for CH_3D and line intensities, broadening coefficients, and rotational assignments for CH_4.

Significant improvements in planetary data are now within reach, so the need for improved laboratory measurements is imminent. Consequently, in this first report in a series of studies of CH_3D under self and foreign gas broadening conditions, we present new measurements of line intensities and self broadening coefficients for the 221 lines of the $3\nu_2$ band of CH_3D that have so far been rotationnally assigned[3]. In addition, we measured intensities and self broadening coefficients for 34 rotationally assigned lines belonging to a second band intermixed with the $3\nu_2$ band. The spectra used for these measurements were recorded at Kitt Peak National Observatory with the Fourier transform infrared spectrometer.

Based on these measurements we have derived a first estimate of the square of the vibrational dipole moment matrix element $|<0|\mu_z|3\nu_2>|^2$: $(8.9\pm0.8)\times10^{-7}$ Debye-squared, leading to a $3\nu_2$ band intensity of $(2.37\pm0.19)\times10^{-21}$ cm⁻¹/(molecule.cm⁻²) at 295K.

[1] - C. de Bergh, B.L. Lutz, T. Owen and J.P. Maillard, Ap.J. 355, 661, 1990
[2] - C. Lecluse, F. Robert, D. Gautier and M. Guiraud, Planet. Space Sci. 44, 1579, 1996
[3] - B.L. Lutz, C. de Bergh and J.P. Maillard, Ap.J. 273, 397, 1983

Time resolved rapid scan FT-UV spectroscopy
and its application to flash photolysis of Br_2 and O_3

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A method for extracting time resolved information from digitally sampled rapid scan interferograms is described. A commercial UV-VIS-Fourier transform spectrometer (BRUKER IFS 120 HR) is used to record time dependent spectra. The observed experiment is triggered at certain positions of the scan mirror, thus receiving time varying interferograms. After processing the obtained set of interferograms time resolved UV-VIS spectra are yielded.

The method is applied to the observation of flash photolysis experiments, stratospheric photochemical reactions being simulated. Gas mixtures of O_3 with Br_2 and Cl_2 are dissociated by a UV-flash. Simultaneously, absorption spectra of the reaction products as well as of intermediate molecular states are recorded.

F33

FERMI RESONANCE $v_3=1/v_5=2$ IN DEUTERATED IODOACETYLENE

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As known from the literature[1,2], the Fermi resonance $v_3=1/v_5=2$ plays an important role when studying heavier halogenated acetylenes. In our laboratory, the energy level system $v_3=1/v_5=2$ has recently been investigated for the normal isotopic species, HCCI, of iodoacetylene[1]. The interaction of the energy levels was found to be very strong; the value $W_F=26.2855$ cm^{-1} was obtained for the coupling element. In the present study, the same Fermi resonance has been investigated in the case of deuterated iodoacetylene DCCI.

The infrared spectrum of DCCI has been measured in the spectral range 230-550 cm^{-1} with a Bruker IFS 120 HR Fourier spectrometer in Oulu with an instrumental resolution of 0.0019 cm^{-1}. The weak fundamental band v_3 and the overtone band $2v_5^0$ are observed at 525.84 cm^{-1} and 474.30 cm^{-1}, respectively. Because there exists also an ℓ type resonance between the states $\Sigma(\ell_5=0)$ and $\Delta(\ell_5=\pm2)$ at the overtone level $v_5=2$, the hot band $2v_5^2-v_5^1$ observed at 247.88 cm^{-1} is also important. In the present study the hot bands of the types $v_3- v_5^1$ and $2v_5^{0,2} - v_5^1$ as well as the direct transitions from the ground state (v_3 and $2v_5^0$) were all simultaneously analysed. In order to obtain information on the vibrational dependence of the Fermi resonance, the next layer of the hot bands $(v_3+v_5)^1 - v_3$, $(v_3+v_5)^1$-$2v_5^{0,2}$ and $3v_5^{1,3}- 2v_5^{0,2}$ was also analysed.

[1] A.-M. Tolonen *et al.*, Mol. Phys., <u>83</u>, 1233-1242 (1994).
[2] O. Vaittinen *et al.*, J. Mol. Spectrosc., <u>167</u>, 55-70 (1994).

HIGH RESOLUTION FTIR STUDY OF SiD_3F.
THE GROUND AND THE v_3 AND v_6 = 1 AND 2 STATES

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FT IR spectra of the prolate symmetric top D_3SiF molecule were recorded in the region of the fundamentals v_3 (A_1, 889.898 cm^{-1}), v_6 (E, 550.453 cm^{-1}) and the overtones $2v_3$ (1769.531 cm^{-1}) and $2v_6$ ($2v_6^{\mp2}$, v_0 = 1101.737 cm^{-1}) with a resolution between 2.4 and 5.0 x 10^{-3} cm^{-1}.

Several thousands of lines spanning J and K values as high as 62 and 39 were assigned and fitted. More than 2000 ground state combination differences formed from v_3 and v_6 transitions were fitted, σ = 0.093 x 10^{-3} cm^{-1}, to yield accurate J-dependent ground state rotational constants up to sextic terms, which were furthermore improved by merge with 55 recently measured [1] and appropriately weighted mmw transitions.

The v_3 and $2v_3$ bands were fitted employing a perturbation-free model. The respective rms deviations of 0.11 and 0.28 x 10^{-3} cm^{-1} correspond to the quality of the data.

As for v_6, $\ell(2, 2)$ and $\ell(2, -4)$ innervibrational resonances were taken into account, and a rms deviation of 0.17 x 10^{-3} cm^{-1} was obtained. The $2v_6^{\mp2}$ fit considered $\ell(2, 2)$ interactions with $2v_6^0$ and converged with σ = 0.37 x 10^{-3} cm^{-1}.

The determination of the K-dependent ground state rotational parameters A_0 and $D_{K,0}$ from v_6, $2v_6^{\mp2}$, and $2v_6^{\pm2}$ - $v_6^{\pm1}$ is on the way. Their knowledge is also essential for the analysis of the x,y-Coriolis interacting v_2 and v_5 fundamentals near 700 cm^{-1}, the study of which has been started as well.

In addition, J-dependent ground state parameters of the ^{29}Si isotopomer have been obtained.

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[1] J. Demaison, private communication.

DETERMINATION OF THE NaKr $X^2\Sigma$ AND THE KAr $B^2\Sigma$ INTERATOMIC POTENTIAL FROM LASERSPECTROSCOPIC DATA

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The interatomic potentials of the molecular states $X^2\Sigma$ of NaAr and $B^2\Sigma$ of KAr have been determined in form of an analytical function by means of a standard fit routine fitting the observed energy values of the rovibrational levels to the energies calculated from the potential. For both states all experimental data could successfully be reproduced by using a Hartree-Fock-Dispersion (HFD) function.

For the $X^2\Sigma$ state of NaAr the input data consisted of 104 energy levels observed in our previous laserspectroscopic work [1]. In addition, our recent experimental result for the spectral distribution of the $A^2\Pi \rightarrow X^2\Sigma$ fluorescence was included providing information on the repulsive part of the potential up to 2000 cm^{-1}. Our interatomic potential (with $D_e = 41.6(7)$ cm^{-1} and $R_e = 5.01(2)$ Å) is in very good agreement with the result of a recent theoretical calculation using the concept of the core polarization potential [2].

For the $B^2\Sigma$ state of KAr the energies of 52 bound rovibrational levels with $v = 0...3$ and $J = 0...16$ have been used as input data and are reproduced within a margin of $9 \cdot 10^{-3}$ cm^{-1}. Our preliminary values for D_e and R_e are 9.7 cm^{-1} and 8.02 Å, respectively. However, our present $B^2\Sigma$ potential doesn't take account of the spin-orbit interaction between $B^2\Sigma$ and $A^2\Pi_{1/2}$ which is not negligible. Improved calculations are currently performed in our group.

[1]   G. Aepfelbach et al., Chem. Phys. Lett. 96 (1983) 311
[2]   C. Kerner, Ph.D. Thesis 1995, Universität Kaiserslautern, Germany

F36

CALCULATION OF FAR-WING LINE SHAPES AND
APPLICATION TO ATMOSPHERIC ABSORPTION SPECTRA

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After reviewing previous theoretical calculations of far-wing line shapes within the quasistatic binary-collision framework, we present a new method and some new results for a molecule-molecule system. In particular, we consider preliminary results for the absorption by CO_2 - CO_2 pairs. This system is important for the atmosphere of Venus where it brackets the atmospheric windows and contributes significantly to the greenhouse heating. Future validation studies for this system and extension to other systems will be discussed briefly.

Sub-Doppler Analysis in Collision Induced Transitions

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We report recent results obtained by using the sub-Doppler double resonance technique (S. Carocci et al, *J. Mol. Spectrosc.* **175**, 62–67 (1996)). By this technique we have obtained a very high accuracy in frequency measurements of rotational and vibrational transitions in CH_3I. The method employs collinear propagation of pump (a CO_2 laser) and probe (a 150 GHz microwave radiation) beams to select a velocity class. Different conditions are possible: if the pump laser is tuned very close to the IR resonance, only molecules with a null velocity component along the laser beam are excited and a single line is obtained, narrower than the Doppler limit. When the laser has a large detuning from the center of the roto-vibrational transition, a splitting of the rotational line is observed into two narrow components, which correspond to the velocities selected by counter- and copropagating radiations. The sensitivity of the technique is so high that we could observe signals caused by collisional transfer from other hyperfine sublevels. When the laser is detuned far off resonance, its frequency may be resonant with a different component of the IR spectrum. In this case collisions may transfer molecules to one of the levels involved in mm-wave transition, so a third (resonant) peak appears at the center of the Doppler doublet. The collisional peak has about the same width as the lines of the nearby doublet, i.e. significantly smaller than the Doppler width. Further increasing the detuning of the laser, splits the collisional peak into a doublet with a separation corresponding to that expected for the detuning from the "parent" IR transition.

FOURIER TRANSFORM SPECTRUM OF ^{18}O AND ^{17}O ENRICHED OCS FROM 1800 TO 4400 cm^{-1}.

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The infrared spectrum of carbonyl sulfide has been recorded from 1800 to 4400 cm^{-1} using a sample with 94 % of 18O and 1.3 % of ^{17}O. The resolution of the Bruker IFS-120 Fourier Transform spectrometer was high enough to yield a resolution close to the Doppler limit. With a pathlength of 64 m., we have used pressures 0.006, 0.06, 0.6, and 5.0 torr respectively.

The wavenumber dispersion is less than 1.0×10-5 cm^{-1} for the best bands. A careful calibration yields absolute uncertainties between 2 and 5×10-5 cm-1 according to the spectral range.

More than 100 bands have been assigned for the following isotopomers[†]: $^{18}O^{12}C^{32}S$, $^{18}O^{12}C^{33}S$, $^{18}O^{12}C^{34}S$, $^{18}O^{12}C^{36}S$, $^{17}O^{12}C^{32}S$, $^{17}O^{12}C^{33}S$, and $^{17}O^{12}C^{34}S$. The ^{13}C isotopomers will be studied later using a sample enriched with both ^{18}O and ^{13}C species. For strong bands, hot bands from states as high as 2100 cm^{-1} have been observed.

We have performed Least-Sqares fits on all the reported bands, to obtain the effective states parameters. Furthermore, the data for each isotopomer have been introduced in the corresponding global analyses which fit simultaneously all data available about the rovibrational energies in the electronic ground state ((W, sub-mmW, IR, and Stark spectra). Those energies are calculated by direct diagonalization of energy matrices which include all off-diagonal terms of the Hamiltonian (anharmonic, (-type, and Stark terms). The corresponding molecular parameters will be presented.

Some considerations about intensities will be reported.

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EFFECT OF SPIN-ORBIT INTERACTION ON ENERGETIC AND RADIATIVE PROPERTIES OF THE D $^1\Pi$, d$^3\Pi$ COMPLEX OF NaK

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A rotationally resolved laser excitation spectra of the $(D^1\Pi\text{-}d^3\Pi)\text{-}X1^1\Sigma^+$ band system of the isotopically substituted NaK molecule measured previously[1] have been deperturbed with respect to spin-orbit interaction in the framework of effective Hamiltonian approach. The perturbed D-d complex was approximated by 4x4 Hamiltonian matrix taking into account direct spin-orbit interaction between $D^1\Pi$ state and $^3\Pi_1$ component of $^3\Pi$ state, as well as an admixture of $^3\Pi_0$ and $^3\Pi_2$ character in the "unperturbed" $^3\Pi_1$ level due to electronic-rotational mixing. The deperturbed term values of the D and d states were used to calculate the Dunham coefficients and rotationless RKR potential energy curves of the present states. The relevant overlap integrals $\langle VD|Vd\rangle$ were estimated to extract electronic parameter of the nondiagonal spin-orbit interaction: $\langle el_{spin-orbit}\rangle/\langle VD|Vd\rangle$. The obtained value (el =4.6(0.3 (cm^{-1}) as well as the diagonal spin-orbit coupling constant A_e=7.0(1.5 (cm^{-1}) of the triplet $^3\Pi$ are in a good agreement with semiempirical estimations derived from a simple single-configuration approximation. Using the obtained RKR potentials and the electronic spin-orbit matrix elements, we solved numerically a set of channel-coupling (CC) radial Schrödinger equations corresponding to a perturbation matrix of the 4x4 dimension. In contrast to the conventional diagonalization of the Hamiltonian matrix the CC approach allowed us to take fully into account the effect of the intramolecular perturbations on the rovibrational wavefunctions. The obtained vibrational wavefunctions have been applied in deperturbation analysis of the experimental relative intensity distributions in the bound-bound $D^1\Pi\text{-}X^1\Sigma^+$ and the bound-free $d^3\Pi\text{-}a^3\Sigma^+$ emissions from the common strongly perturbed levels of the D-d complex. The derived experimental transition dipole moments of the D - X and d- a electronic systems are in a good agreement with highly accurate ab-initio results.

1 P.Kowalczyk; J.Mol.Spectrosc. **136**, 1 (1986)

F40

AN ALTERNATIVE LIGHT SOURCE
FOR THE 7 μm REGION APPLYING
DIFFERENCE-FREQUENCY-GENERATION
IN AgGaSe$_2$

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Up to now in the atmospheric window near 10 μm lead salt diode lasers and CO$_2$-lasers are the most common light sources. An alternative system for this region could be designed applying difference-frequency-generation in non-linear crystals. Whereas for the region near 4 μm AgGaS$_2$ is suitable, for the longer wavelength region AgGaSe$_2$ is available.

In this work first results concerning difference-frequency-generation in the 7 μm region will be presented. Two diode lasers (single mode diode laser at about 1300 nm, external cavity diode laser tunable between 1500 and 1590 nm) were combined in a 40 mm long AgGaSe$_2$-crystal applying 90° non-critical Type I phase matching. The available signal-to-noise ratio was sufficient for first spectroscopic experiments on atmospheric trace gases, e.g. SO$_2$. The spectroscopic features and the capabilites will be discussed.

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G1

CAVITY RING DOWN SPECTROSCOPY

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Application of direct absorption techniques is advantageous in a variety of research fields since quantitative *absolute* concentration data as well as *absolute* frequency dependent absorption cross-sections can be extracted from the measurements. Over the last few years it has been demonstrated that Cavity Ring Down (CRD) spectroscopy is a powerful method to perform direct absorption measurements with pulsed light sources. In the CRD detection scheme the *rate* of absorption rather than the magnitude of absorption of a light pulse coupled into a high-Q optical cavity is measured. The advantage over normal absorption spectroscopy results from (i) the intrinsic insensitivity of the CRD technique to light source intensity fluctuations, and (ii) the extremely long effective path-lengths (many kilometers) that can be realized in stable optical cavities.

In this presentation the operation principle of a 'conventional' CRD experiment using pulsed lasers is described. Since the technique is based on a pulsed measurement, it can be used in combination with pulsed molecular beams and it can also be used to study dynamical processes via time-resolved absorption measurements. CRD spectroscopy has sufficiently matured by now that combining CRD detection schemes with other existing spectroscopic techniques is now being experimented with. In this presentation a pulsed multiplex absorption spectrometer, in which the sensitivity of the CRD absorption detection technique is combined with the multiplex advantage of a Fourier Transform spectrometer, is described. In addition a detection scheme in which the specific advantages of Polarization Spectroscopy and CRD spectroscopy are combined, a detection scheme that offers a significant improvement in sensitivity and utility over the individual methods, is outlined. The possibilities of CRD using a narrowband (quasi)-cw excitation laser for trace gas detection purposes as well as for high resolution spectroscopy will be discussed.

G2

HYDROGEN FLUORIDE CLUSTER DYNAMICS VIA HIGH RESOLUTION IR SPECTROSCOPY: ACHIEVEMENTS, LIMITATIONS AND ALTERNATIVES

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Infrared spectroscopy is a key technique for the study of hydrogen bonds. Rotationally resolved spectra have unravelled the hydrogen bond structure, energetics and dynamics of the simple prototype $(HF)_2$ in unprecedented detail. The first part of the lecture will highlight some recent results of different research groups[1], which culminate in the development and testing of an accurate analytical potential energy hypersurface for two HF molecules[2].

Because of cooperative contributions to hydrogen bonding, the potential energy hypersurface of the dimer by no means contains the full information on larger clusters[3]. Depending on cluster size and frequency range, high resolution IR spectroscopy runs into practical and fundamental limitations for these larger systems[3]. It will be demonstrated how a combination of vibrationally resolved supersonic jet FTIR spectroscopy, quantum chemistry, and nuclear quantum dynamical calculations provides an accurate description of hydrogen bonding in $(HF)_n$ clusters[3] with n up to 8. Finally, spectral changes observed for clusters with $n \gg 8$ are discussed[4].

[1] A.S. Pine, W.J. Lafferty, B.J. Howard, *J. Chem. Phys.* **81** (1984) 2939; K.v. Puttkamer, M. Quack, *Chem. Phys.* **139** (1989) 31; M. Quack, M. A. Suhm, *Chem. Phys. Lett.* **171** (1990) 517; D.J. Nesbitt / R.J. Bemish, M. Wu, R.E. Miller / H.C. Chang, W. Klemperer; *Faraday Discuss.* **97** (1994) 1 / 57 / 95; R. Signorell, Y. He, H.B. Müller, M. Quack, M.A. Suhm, *Proceedings of the 10th International Symposium on Atomic, Molecular, Cluster, Ion, and Surface Physics*, 256. Vdf Publishers, Zürich, 1996.
[2] W. Klopper, M. Quack, M. A. Suhm, *Chem. Phys. Lett.* **261** (1996) 35.
[3] M. Quack, J. Stohner, M.A. Suhm, *J. Mol. Struct.* **294** (1993) 33; M.A. Suhm, J.T. Farrell, Jr., S. Ashworth, D.N. Nesbitt, *J. Chem. Phys.* **98** (1993) 5985; D. Luckhaus, M. Quack, U. Schmitt, M.A. Suhm, *Ber. Bunsenges. Phys. Chem.* **99** (1995) 457; M.A. Suhm, *Ber. Bunsenges. Phys. Chem.* **99** (1995) 1159: M. Quack and M. A. Suhm. In Jean-Louis Calais and Eugene S. Kryachko, editors, *Conceptual Perspectives in Quantum Chemistry*, p. 417, Kluwer, Dordrecht, 1997.
[4] M. Quack, U. Schmitt, M.A. Suhm, *Chem. Phys. Lett.*, **269** (1997) 29.

H1

FIRST MICROWAVE TRANSITIONS OF A NEGATIVE ION
SH⁻ AND SD⁻

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Although the infrared spectra of several negative ions has been measured no microwave data is available that would allow a search for these ions in space. This lack is probably due to a combination of problems involving production conditions, need for a wide spectral coverage and most importantly identification. We produced SH⁻ and SD⁻ using an electrical discharge in H_2S and argon buffer gas and measured three transitions of these ions using the Lille microwave spectrometer whose frequency range has recently been extended towards 1 THz using Russian-constructed BWO tubes. Firm identification of negative ions was carried out by studying the effect of Doppler line-shifting due to acceleration of the ions in the electric field of the positive-column discharge. Two sets of data were taken with the position of the detector and BWO tube interchanged. Line frequencies of neutral molecules were not affected, SH_3^+ was shifted by about 200 kHz between the two setups and negative ions were shifted in the opposite direction.

H2

THE IMPORTANCE OF THE HIGHER INTERRELATIONS
OF THE DUNHAM COEFFICIENTS

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The formulae describing the exact interrelations of the Dunham coefficients upto 20-th order have been published recently[1].

The calculations with the use of these formulae for different indices k and l are presented.

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[1] -M. Rytel and T. Rytel, *J. Mol. Spectrosc.* (in press).

High Resolution Mid-Infrared Molecular Absorption Spectroscopy of Collisionally Cooled Hydrofluorocarbon Vapours

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Rotationally and vibrationally cooled (below 100 K) high resolution (up to 0.004 cm^{-1}) mid-infrared gas-phase spectra of three hydrofluorocarbons (difluoromethane (CH_2F_2), trifluoromethane (CHF_3) and 1,1,1–trifluoroethane (CH_3CF_3)) have been obtained using a Bruker IFS 120HR Fourier transform spectrometer and a collisional cooling (or "diffusive trapping") technique at the Molecular Spectroscopy Facility of the Rutherford Appleton Laboratory. To demonstrate the applicability of this technique to the simplification of dense molecular absorption features, the collisionally cooled spectra are compared with higher resolution (up to 0.0016 cm^{-1}) measurements of the gases in conventionally cooled gas cells at 296 and 200 K. The supression of thermally populated vibrational states in the collisionally cooled spectra was particularly evident. The advantages of this technique over supersonic jet spectroscopy are discussed. Spectral features arising from the formation of hydrofluorocarbon molecular clusters were also observed.

H4

CAVITY RING DOWN SPECTROSCOPY
ON TRANSIENT SPECIES

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Cavity ring down (CRD) spectroscopy has proven to be a good probe to detect weak molecular transitions or species that are hard to produce in high abundances. By combining a CRD unit with a hollow cathode discharge, very long absorption path lengths (up to 40 km) have been achieved, and it will be demonstrated here that this technique is suited to detect transient species in an ultrasensitive way. The first electronic gas phase spectra of C_6H will be presented, as well as preliminary results on longer carbon chains. These molecules are thought to play a role as carrier of some of the diffuse interstellar bands. Furthermore, it will be shown that this technique offers a good possibility to detect both positive and negative ions. For C_2^- even a lower detection limit of 10^7 ions/cm^{-3} has been estimated. Finally the first results will be shown of a newly operational supersonic slit jet discharge system in combination with a CRD set-up.

H5

A JET FTIR SPECTROMETER FOR THE
DETECTION OF WEAK ABSORPTION BANDS

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We used the combination of a Fourier transform interferometer with a large slit-jet[1] to record weak absorption bands such as overtone and combination bands of medium sized molecules. Under typical conditions, the jet is produced from a 16 cm long, 30 micron wide slit at a stagnation pressure of less then 1 atm. Initially gaseous and liquid samples can be handled. The set-up will be described in detail and its performance illustrated by new, unpublished results to be further detailed in other contributions to the meeting.

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H6

Molecular beam FT-microwave spectroscopy
- Stark effect -

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The knowledge of dipole moments supports the understanding of structure and dynamics of molecular clusters. Especially when the accurate rotational constants obtained from microwave spectroscopy do not lead to an univocal structure determination, electric dipole moment measurements can play a very important role.

The application of the Stark effect to the dipole moment determination using a molecular beam Fourier transform microwave (MB-FTMW) spectrometer goes back to about 10 years ago, when the NIST group at Gaithersburg determined the dipole moment of the water dimer [1]. Briefly, in the conventional setup for Stark measurements, the experiments are performed with the pulsed molecular beam perpendicular to the resonator axis [2].

Here the first successful attempt to perform Stark measurements in the MB-FTMW spectrometer [3] using the new geometry with parallel molecular beam and resonator axis is reported. This provides advantages over a perpendicular setup, improving resolution and sensitivity. Moreover the aluminum Stark plates are coated with a microwave absorber. Low frequency modes are still present in the cavity, and, as a positive side effect, unwanted modes are quenched. Calibration of the system and preliminary results will be discussed.

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Ultra-fine Structure in the λ5797 Diffuse Interstellar Absorption Band.

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The origin of the diffuse interstellar absorption bands, which now number over 150, is the longest standing problem in astrophysical spectroscopy. Even the question as to whether the bands arise in dust grains or free gas phase molecules has not yet been settled. We report high resolution and high signal-to-noise observations of the λ5797 diffuse interstellar absorption band, recorded with the Ultra-high Resolution Facility at the Anglo-Australian telescope and the Kitt Peak National Observatory 0.9 m coudé feed telescope. With careful choice of targets and at a resolving power of up to 600 000, a hitherto unexpected high level of fine structure, which is intrinsic to the band, is observed along different lines of sight. The structure is reminiscent of that arising from a partially resolved molecular electronic transition.

Under the assumption of a molecular carrier, rotational contour fitting of the profile yields molecular parameters which are consistent with the spectrum arising from an electronic transition in a large, probably carbon-based, molecule. Plausible candidates are discussed.

H8

N_2-, O_2-, AND AIR-BROADENING COEFFICIENTS OF WATER VAPOR

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The pressure broadening of two rotational lines of water vapor by nitrogen and oxygen have been analyzed: the 3_{13}-2_{20} line of $H_2^{18}O$ near 203 GHz and the 5_{14}-4_{22} line of $H_2^{16}O$ near 325 GHz. The experiments were performed with a millimeterwave spectrometer using multiplied klystrons as sources and a bolometric detection. Partial pressures of the perturber gas between 0 and 400 mTorr were considered.

The broadening coefficients for O_2 and N_2 were determined at several temperatures between 273 and 393K, leading to the determination of the temperature dependence exponent of these coefficients.

Air broadening parameters were retrieved from N_2 and O_2 results, in order to provide confident data for future satellite programs dedicated to the sounding of the atmosphere.

H9

PHOTODISSOCIATION DYNAMICS OF T-BUTYL NITRITE

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The photodissociation dynamics of alkyl nitrites in the near-UV have been the subject of intense theoretical and experimental investigation in recent years. The work to be reported in the poster focuses on the 355 nm photodissociation of jet-cooled t-butyl nitrite - $(CH_3)_3CONO$. The rotational alignment parameter, $A_o^{(2)}$, for the NO photofragment has been measured in a jet. The alignment values reach a high-J limit of +0.25 when probing the NO photofragment in its $v''=0$ state and +0.42 when probing NO ($v''=1$). The alignment value will be discussed in the context of a prompt, direct and vibrationally adiabatic dissociation mechanism in which the rotation vector, **J**, of the NO photofragment and the transition dipole moment, μ of the $S_1(n\pi^*) \leftarrow S_0$ transition are preferentially aligned parallel. The vibrational and rotational state distribution of the NO fragment produced by 355 nm photolysis of the jet-cooled parent will also be discussed.

The gas-phase, room temperature electronic absorption spectrum will be presented and the widths of the prominent bands compared to those of the photofragment yield spectra and of absorption spectra recorded in an argon matrix. The bands in the 10 K photofragment yield spectrum are wider than in the 300 K absorption spectrum Our conclusions from these results will be presented in the poster.

H10

N_2 LINESHIFT COEFFICIENTS IN THE ν_2 WATER VAPOR BAND

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The measurements of the nitrogen broadened water vapor lineshift coefficients in the 1850 -2230 cm^{-1} spectral region were made with the Fourier transform spectrometer at the Laboratoire de Physique Moleculaire at Applications of the University of Paris. The spectral resolution was 0.005 cm^{-1} and the nine spectra at different pressures of sample mixtures (at the room temperature) have been recorded. Two independent procedures have been used to obtain the line shift coefficients: in the first procedure the shift was calculated as a difference between absorption maxima in the two spectra recorded with and out the buffer gas, in the second method the line center determinations were made by nonlinear least-square fitting of the Voigt contour to the measured values of transmittance. Accuracy in the determination of line shift coefficient was estimated to be better than 1 mK/atm (1 $mK=10^{-3}cm^{-1}$). The lineshift coefficients have been determined for 150 well resolved and isolated lines of R-branch of the ν_2 band with high quantum numbers J up to 16 (Ka = 0,...,8). Their values range from +15 to -29.3 mK/atm. Calculations were performed using the ATC - theory and cut-of-free method. Dipole-quadrupole, quadrupole-quadrupole, induction and dispersive interactions were taken in the calculations. Fairly satisfactory agreement between measured and calculated line shift coefficients has been found.

COMPLETE THEORETICAL ANALYSIS OF THE FIRST DECADE OF THE $H_2^{18}O$ INTERACTING VIBRATIONAL STATES: LINE POSITIONS AND INTENSITIES

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Fourier transform spectra of ^{18}O-enriched water vapor recorded between 9500 and 11500 cm^{-1} in Ref.[1] have been reanalyzed, yielding 656 precise vibro-rotational energy levels, which were fitted to the Pade-Borel effective Hamiltonian with a RMS deviation of 0.022 cm^{-1} using 127 adjusted parameters. The effective transition moment parameters have been obtained for the 1st decade vibrational states from the fitting of more than 1100 experimental line intensities, with a RMS deviation of 3.8% .

Finally some energy levels of the highly excited (070) state have been derived from the experimental lines borrowing their intensities due to strong resonance interactions with the (220) and (121) states.

Acknowledgment

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LINE SHIFT INVESTIGATIONS
IN THE ν_2 BAND OF H_2S

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After publishing recently data concerning line broadening in all fundamental bands of H_2S[1,2,3] in this paper for the first time line shift coefficients for several lines from the ν_2 band of H_2S in the region between 1080 cm^{-1} and 1340 cm^{-1} will be presented. Lines from all branches within the quantum number intervals $(3 \leq J'' \leq 11)$, $(0 \leq K_a'' \leq 5)$ were studied with helium, neon, argon, krypton, xenon, nitrogen, oxygen, hydrogen, deuterium, and carbon dioxide as perturber. The characteristics of the quantum number dependencies of the shift and the perturber dependence will be discussed and compared to other perturbers.

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H13

A Theoretical Calculation of the Absorption Spectrum of CH_2^+

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The ground $\widetilde{X}$ $^2A_1$ electronic state of CH_2^+ is quasilinear with a small barrier to linearity, and at linearity the state becomes degenerate with the $\widetilde{A}$ $^2B_1$ electronic state forming a $^2\Pi_u$ state. Hence these two states are subject to the Renner effect. We have already calculated the rovibronic energies of the states using *ab initio* potential energy surfaces that we generated (P. Jensen, M. Brumm, W. P. Kraemer, and P. R. Bunker, J. Mol. Spectrosc. 172 (1995) 194). In the present work we use the electronic wavefunctions of the previous *ab initio* calculation to determine the dipole moment and transition moment surfaces, and we develop the theory that allows us to use these to calculate intensities. As a result we now calculate both the positions and intensities of the lines in the absorption spectrum of CH_2^+, and its deuterated isotopomers, making full allowance for the effects of the Renner interaction and of spin-orbit coupling. We predict the appearance of the absorption spectrum over the whole wavenumber range from 0 cm^{-1} to beyond 15 000 cm^{-1}; this involves only the $\widetilde{X}$ and $\widetilde{A}$ electronic states. We hope that these results allow experimentalists to search successfully for the features that we predict.

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H14

SPATIAL LOCALIZATION OF WAVE PACKETS
COMPOSED OF MANY VIBRATIONAL STATES

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Wave packets excited by ultrashort femtosecond light pulses in diatomic molecules are composed of many vibrational components. We obtained approximate closed-form expression for such packets using the Green's function approach combined with the primitive semiclassical representation of stationary wave functions. We showed that only few of many vibrational components contribute to wave packet at a given moment and position.

To check the accuracy of semiclassical approximation, we considered the limiting case of infinitely short (δ-like) light pulse. The diatomic molecule was represented by a model of two displaced harmonic oscillators with different frequencies. Three parameters appear in this model: the potential displacement R, the ratio of the upper and lower oscillator frequencies ω, and the vibrational quantum number of the initial oscillator. The closed-form expression for the wave packet excited from an arbitrary initial level was obtained using the generating function, which has the following form:

$$F(x,t,z) = \frac{1}{\sqrt{\pi\sigma(t)}\sqrt{1-z^2}} \exp\left\{-\frac{[x+R\cos(\omega t)]^2}{\sigma(t)}\frac{1-z}{1+z}\right\}$$

where $\sigma(t) = \cos^2(\omega t) + \frac{1}{\omega^2}\sin^2(\omega t)$ is the spatial width of the moving packet.

Combining the results of semiclassical approximation and the exactly solvable model, we studied the effect of pulse shortening on the spatial width of the packet. If the light pulse is short enough, so that its spectral width covers the spectral width of the packet, further shortening of the pulse will give no result. Therefore, for any given potentials, there exists some limiting pulse duration (which is small, but finite), when the pulse forms the packet that is identical to the packet formed by an infinitely short pulse.

MODELING AT THE *AB INITIO* LIMIT

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The convergence of *ab initio* predictions to the one- and n-particle limits is systematically explored for several benchmarks of inversion barriers, torsional barriers, barriers to linearity, and other conformational features. Explicit *ab initio* results are obtained with atomic-orbital valence basis sets as large as $(7s6p5d4f3g2h1i)$ and electron correlation treatments as extensive as CCSDT. A subsequent extrapolation is employed to arrive at the *ab initio* limit.

Physical effects which are tacitly neglected in most theoretical work are also quantified by computations of core-core and core-valance correlation, relativistic, and non-Born-Oppenheimer (BODC) shifts of conformational energies and barriers.

The design of the research is not only to establish more definitive standards for precise theoretical predictions in conformational and large-amplitude motion energetics but also to further refine key energetic quantities for molecular prototypes in this field of investigation.

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H16

ROTATIONAL ANALYSIS OF THE WEAK BENDING OVERTONES nv_2 (n=2,3) OF THE HDS MOLECULE

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There were two main goals of present study: 1) to obtain simple relations which would allow the prediction of spectroscopic parameters and rotational energies of bending overtones of XHD-type isotopic species on the basis of information about spectroscopic parameters of XH_2-type molecules (for symmetric XD_2 species such a problem was solved on the basis of results of the Isotope Substitution Method, Ref.[1]. However, in general case, for non-symmetric XH_2 $\rightarrow$ XHD substitution, corresponding relations cannot be obtained); 2).on this basis to analyse rotational structures of weak rotation vibrational bands $2v_2$ and $3v_2$ of the HDS molecule.

On the basis of the "expanded local mode approach", which we derived earlier Ref.[2], isotopic relations were developed for the harmonic ω_2 and anharmonic x_{22} vibrational parameters, the equilibrium rotational B_a^e and vibration-rotational α_λ^β constants, centrifugal distortion parameters, which allow us to predict with satisfactory accuracy line positions in the weak absorption bands $2v_2$ and $3v_2$ of the HDS molecule.

High resolution spectra of these overtone bands were recorded on the Bruker IFS 120HR Fourier transform spectrometer (Oulu, Finland) and analysed in the regions of 1800-2050 cm^{-1} and 3050-3200 cm^{-1}, respectively In spite of very weak absorption, assignments of lines have been made on the basis of theoretical predictions using the above mentioned isotopic relations. A set of rotational and centrifugal distortion parameters was obtained which a).reproduces the initial experimental data with mean accuracies of 0.0002 cm^{-1} b) lies close to the values predicted on the basis of isotopic relations.

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COUPLED CLUSTER CALCULATIONS FOR THREE LOW-LYING DOUBLET STATES OF LINEAR C_{10}^-

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Making use of a large basis set of 270 contracted Gaussian-type orbitals partially restricted coupled-cluster calculations including connected triple substitutions in a perturbative way (RCCSD(T)) have been carried out for three low-lying doublet states ($^2\Pi_u$, $^2\Sigma_g^+$ and $^2\Pi_g$) of linear C_{10}^-. The calculated T_e value for the $^2\Pi_g$ state is 10 890 cm^{-1}, in close agreement with the T_o value of 10 338 cm^{-1} obtained by absorption spectroscopy in a neon matrix.[1] According to our calculations, the observed peaks at 12 330 and 12 430 cm^{-1} have to be assigned to the 2_0^1 and 1_0^1 transitions. The assignment of the peak at 10 826 cm^{-1} is unclear, but it certainly does not correspond to the 4_0^1 transition.

For the $^2\Sigma_g^+$ state, we predict a T_e value of 9 951 cm^{-1}. Besides the adiabatic peak, the 2_0^1 transition shows up strongest in the absorption spectrum.

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CONFORMATIONALLY INDUCED ROTATIONS OF THE MOLECULAR ELECTRONIC TRANSITION MOMENTS IN SUBSTITUTED BENZENES. A COMBINED EXPERIMENTAL AND THEORETICAL STUDY.*

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Aromatic molecules substituted with flexible side chains may be stabilized in a number of different conformations in the low temperature environment of a supersonic free jet [1]. Recently, it has been discovered that the different conformations of several substituted benzenes exhibit differently oriented SI - SO optical transition moments (TM's) in the molecular frame [2]. Typically the SI-S0 TM's of anti conformers lie along the b axis, perpendicular to the point of attachment of the substituent to the ring, whereas the corresponding TM's of gauche conformers make angles of up to 60 deg width the b axis. The observed orientations have also been found to be extremely sensitive to the nature of the attached group, to subtle changes in its position with respect to the aromatic ring, and to complex formation 13]. The rotation angles also are sensitive to the conformation of the terminal group when there is the possibility of intermolecular hydrogen bonding and/or intramolecular interactions between centers of high electron density. In this report, we shall give a summary of the experimental data obtained to date and offer a theoretical model that account' for them. The results provide an intriguing view of aromatic ring-side chair interactions and their influence on the photophysical and photochemical properties of the light absorbing species.

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HIGH RESOLUTION LASER SPECTROSCOPY
OF THE ^{23}Na^{39}K $B^1\Pi$ STATE :
PERTURBATION AND PREDISSOCIATION
NEAR DISSOCIATION LIMIT

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High resolution spectra of the ^{23}Na^{39}K $B^1\Pi(v', J') - X^1\Sigma^{o+}(v'', J')$ transitions were measured up to the breaking-off points, where NaK dissociates to the Na($3s^2S_{1/2}$) + K($4p^2P_{3/2}$) atoms, by the technique of Doppler-free optical-optical double resonance polarization spectroscopy.

The (v, J) dependencies of energy and line width of the transitions to the $B^1\Pi(v=30-43, J)$ levels are studied, a number of transition lines are found to be perturbed and/or broadened. Line broadenings are observed for transitions to the $B^1\Pi(v=30, J=42)$, $(v=31, J=35)$, $(v=32, J=27)$, $(v=33, J=14)$, and $(v=34, \text{all } J)$ levels, and are attributed to the predissociation via the $c^3\Sigma^{o+}$ state to the Na($3s^2S_{1/2}$) + K($4p^2P_{1/2}$) atoms. Below and near the predissociation threshold, a series of the perturbation centers which converge to the predissociation threshold is observed for each v, and the perturbing state is identified as the $c^3\Sigma^{o+}$ state. Another rotational perturbations are observed also above the predissociation threshold, and the perturbing state is identified as the $b^3\Pi_1$ state. In this case, the line widths are observed to change drastically around the maximum perturbation, and this is identified as originating from the interference effect which arises because both the $B^1\Pi$ and $b^3\Pi_1$ states interact with the dissociative continuum of the $c^3\Sigma^{o+}$ state. Such an interference effect is universal, and it would be important for further understanding of chemical reactions.

RENNER-TELLER EFFECT IN THE $X^2\Pi_{g(3/2)}$ $(v_1, 2^l, 0)$ LEVELS OF CuCl$_2$

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The Laser Induced Fluorescence spectra of CuCl$_2$ have been recorded by Fourier transform spectroscopy in the gas phase both in cell and molecular beam conditions. The spectra show transitions to combination levels of the symmetrical (ν_1) and antisymmetrical (ν_3) stretching modes and of the bending mode ($\nu_2 = 2$) in the electronic ground state $X^2\Pi_{g(3/2)}$. The bending levels are affected by the Renner-Teller effect and show the K-type doubling.

We have constructed an effective hamiltonian by using degenerate perturbation theory. We have calculated the matrix elements up to the 3rd order, in a parity-conserving Hund's case (a) basis set. The spin-orbit splitting was included in the $zero^{th}$ order ($|A_{SO}| > \omega_2$). We took the rotation ($6.5 \leq J \leq 80.5$) and the K-type doubling into account. Non-linear, least squares fits have been performed for $^{63}Cu^{37}Cl_2$ in the bands $(v_1, 2, 0)$ $v_1 = 0$ to 6 and for $^{63}Cu^{37}Cl_2$ (020). From these, we have obtained the vibrational energy G_2, the rotational and centrifugal distortion constants B and D, the Λ- and K-type doubling parameters p_2, q_2, the Renner and vibronic parameters $\epsilon\omega_2$, g_K for these levels.

FREE JET ABSORPTION MILLIMETER WAVE SPECTROSCOPY OF COMPLEXES OF SATURATED 5-MEMBERED RINGS WITH ARGON: 1,3-DIOXOLANE-Ar AND TETRAHYDROFURAN-Ar

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The rotational spectra of both 1,3-dioxolane and tetrahydrofuran are characterized by large splittings due to the ring "pseudorotation". Rather surprisingly the free jet spectra of the corresponding adducts with argon exhibit different behaviours: the spectrum of tetrahydrofuran-Ar is characterized by systematic line doubling, while this does not happen for dioxolane-Ar.

INVESTIGATION OF THE TORSIONAL FAR-INFRARED OVERTONES AND HOT BANDS OF ACETALDEHYDE AND INTERACTIONS WITH THE ν_{10} FUNDAMENTAL BAND

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The torsional overtone spectrum of CH_3CHO has been recorded with a high resolution (0.003 cm^{-1}) Far-Infrared Fourier Transform spectrometer, between 40 and 90 cm^{-1} and between 180 and 230 cm^{-1}. This spectrum completes the far-infrared spectrum recorded a few years ago from 80 to 180 cm^{-1} to study the fundamental torsional band $v_t = 1-0$ and the two first overtones $v_t = 2-1$ and $3-2^1$. The spectral region between 40 and 90 cm^{-1} is very dense and allows us to assign many $v_t = 2-1$ lines and $v_t = 3-2$ lines. The region between 180 and 230 cm^{-1}, on the other hand, is less congested and allows us to search for weaker lines from the $v_t = 3-1$ and $4-2$ overtone bands. The spectrum of the ν_{10} band was recorded last year at high resolution with a Fourier Transform spectrometer in the region of 450 to 550 cm^{-1} region and partly assigned. A number of strong perturbations arising likely from interactions with the $v_t = 4$ torsional levels of the ground state were observed. As a first step to investigate doorway states which facilitate passage of energy from the small amplitude manifold to the torsional manifold, the goal of this study is to consider a two-by-two theoretical model involving both ν_{10} and the ground vibrational state and to carry out a simultaneous fit of the perturbed lines from $v_{10}=1$ and from vt=4 of the vibrational ground state.

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[1]I. Kleiner, J. Hougen, J-U. Grabow, S. P. Belov, M. Yu. Tretyakov and J. Cosléou

H23

HIGH SENSITIVITY DETECTION OF THE ROTATION SPECTRUM
OF HYDROGEN HALIDES IN THE V = 1 STATE BY TUNABLE FIR
SPECTROSCOPY

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We have observed for the first time in absorption several rotational
transitions in the first excited vibrational state of a series of halides: $H^{35}Cl$,
$H^{37}Cl$, $D^{35}Cl$, $D^{37}Cl$, $H^{79}Br$, $H^{81}Br$, $D^{79}Br$ and $D^{81}Br$.

A tunable FIR Spectrometer was used with a multiple-pass cell to improve
the sensitivity. The experimental problems connected with the measurements
will be illustrated. The hyperfine structure of the transitions has been partially
resolved at low J values for the bromine containing molecules only.

H24

AB INITIO STUDY AND
MILLIMETER-WAVE SPECTROSCOPY OF P_2O

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The millimeter-wave spectrum of P_2O, produced by reacting P_4 vapour with atomic or molecular oxygen directly inside the absorption cell, has been observed in 13 vibrational states.

Reliable identification of the various vibrationally excited states has been achieved with the help of high-level *ab initio* calculations resulting in accurate geometric data and an anharmonic force field.

Careful analysis of the vibrational levels observed resulted in 13 sets of rotational and centrifugal distortion parameters, which have been used, in turn, to determine the equilibrium rotational, quartic centrifugal distortion, and rovibrational interaction constants of P_2O.

A preliminary analysis of a Fermi resonance between $2\nu_1$ and ν_3 will be presented.

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HIGH RESOLUTION FTIR SPECTRUM OF THE ν_3, ν_4, AND ν_5 BANDS OF DCCBr

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The high resolution vibration-rotation spectrum of deuterated monobromo-acetylene (DCCBr) has been recorded in the wavenumber region 240 - 650 cm^{-1}. The measurements have been carried out with Bruker IFS 120 HR spectrometers both in Wuppertal and in Helsinki at a resolution of about 0.003 cm^{-1}. The recorded spectra show a congested fine structure due to the two isotopic species, $DCC^{79}Br$ and $DCC^{81}Br$, and due to numerous hot, overtone, summation, and difference bands. The observed ν_3 (CBr stretch), ν_4 (CCD bend), and ν_5 (CCBr bend) band systems have been rotationally analysed. The analysis has provided parameters altogether for about 50 vibration-rotation bands. Furthermore, an anharmonic Fermi resonance model based on normal coordinates has been applied to explain the observed vibrational perturbations and to reproduce the observed term values and rotational constants. By using the model we have constructed the energy level scheme of the vibrational states of DCCBr below 1500 cm^{-1}.

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NEW HIGH RESOLUTION ANALYSIS OF H_2CO IN THE 3.6 and 4.3μm
REGION BY FOURIER TRANSFORM SPECTROSCOPY

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Using new Fourier transform spectra recorded at high resolution at LPMA
Paris, it has been possible to perform a new study of the formaldehyde
absorption spectra in the $2600\text{-}3000\text{cm}^{-1}$ and in the $2200\text{-}2500\text{cm}^{-1}$
spectral ranges. This analysis was started using the results obtained by
previous studies performed in the same spectral regions [1,2]. In the high
frequency range, the analysis of the strongest bands, namely ν_1 and ν_5
(symmetric and antisymmetric stretching modes) was complicated by the
existence of Fermi-type resonances and by A-type, B-type and C-type
Coriolis interactions involving the ν_1 and ν_5 energy levels and levels from
various overtone or combination states namely $\nu_2+\nu_6$, $2\nu_3$, $\nu_2+\nu_4$, $\nu_3+\nu_6$
and $\nu_3+\nu_4$. In the low frequency range, which involve the weak $2\nu_4$ and $2\nu_6$
bands and the very weak $\nu_4+\nu_6$ band, the $v_4 = 2 \leftrightarrow v_6 = 2$ Fermi type
resonance and the $v_4 = 2 \leftrightarrow v_4 = 1, v_6 = 1$ and $v_6 = 2 \leftrightarrow v_4 = 1, v_6 = 1$
A-type Coriolis interaction had to be considered. For each analysed spectral
region, a preliminary calculation of the energy levels was performed taking
into account the observed resonances. It appears that these two spectral
domains should not be considered as independent because of the existence
of additional resonances linking levels measured in each spectral region.

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An Emission Measurement of Bending Mode Hot Bands of $D^{13}C^{15}N$

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We have measured the threefold substituted HCN isotopomer $D^{13}C^{15}N$ in an emission experiment at 1400 K in the range from 400 to 750 cm^{-1}. The setup is described elsewhere[1].

We could assign bending mode bands up to $v_2'=11^{11}$. The assignments have been verified for states up to $v_2=6$ by their agreement with levels obtained from earlier measurements of overtone and hot bands of the $2v_2$ region. For higher states the assignments are confirmed by the consistent results of a least squares fit.

All of the measurements involving the bending vibrational states have been included in a single fit that includes approximately 2000 transitions which have an rms deviation on the order of 0.0005 cm^{-1}. No lines were included in the fit unless they are within ±0.001 cm^{-1} of the calculated values and have roughly the expected intensity. In many cases the assignments could be verified by the splitting of certain levels that can be resolved at sufficiently high J values.

The l-type resonance-corrected rovibrational constants of the bending states $v_2=1,...,11$ are reported, as well as those of some combination states with the CN stretching mode.

We believe that we are able to see very high bending states because of the so-called vibrational Hönl-London constants for a linear molecule, which are given in[2]. One could also think of these high hot bands as $K \rightarrow K+1$ transitions for an asymmetric rotor or for a symmetric top.

[1] Poster: G. Ch. Mellau, M. Winnewisser, High S/N FTIR Emission Setup for the Range 300-11000 cm^{-1}
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H28

High resolution zero-kinetic-energy photoelectron spectra in the 16-20 eV photon energy range

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A new molecular beam apparatus has recently become operational in Zürich to study the pulsed field ionisation of atoms and molecules, which have been photoexcited to high Rydberg states. Coherent XUV radiation is generated by four-wave mixing of the doubled or tripled outputs of two dye lasers, which are simultaneously pumped by a Nd:YAG laser.

Amoung others, the set-up has been used to determine the structure of the ND_4 radical[1] and to investigate the effects of ions on the pulsed field ionisation behaviour of high Rydberg states.[2]

Here we will present new experimental results using XUV radiation in the 16-20 eV photon energy range.

[1] J. Chem. Phys. **106**, 6523-6533 (1997)
[2] Chem. Phys. Lett. **270**, 1-8 (1997)

The Intrinsic Torsional Splitting of Ethane.

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We call "intrinsic" the torsional splitting in an isolated vibrational state of etane, free from perturbations. The intrinsic splitting increases with the excited torsional quanta v_4, and is expected to become detectable under a Doppler limited resolution at $v_4=1$ in C_2H_6 and at $v_4=2$ in C_2D_6. We have shown that the degenerate normal modes of ethane occur in E_{1d},E_{2d} pairs[1], and the intrinsic torsional splitting in E_{1d},E_{2d} states is expected to follow the same pattern as in non-degenerate vibrational states. However the γ-Coriolis mixing of E_{1d} and E_{2d} vibrational states differing by one quantum of v_4 affects the torsional splitting and also contributes to alter the intrinsic splitting. By a simplified procedure we concluded that the torsional splitting is expected to decrease drastically in a degenerate vibrational state as the Coriolis coefficient approaches the value of -0.5, as in the degenerate methyl deformation modes v_8 and v_{11} ($\zeta=\sim-0.4$). This is confirmed by the observation in $2v_4+v_{11}$ of C_2D_6[2], but not in v_4+v_8 of C_2H_6[1]. Further work is in progress to clarify the torsional splitting mechanism in degenerate vibrational states.

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H30

THE FIRST STRETCHING OVERTONE OF H_3SiD.
EMERGENCE OF LOCAL MODE EFFECTS

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The FTIR spectrum of H_3SiD in the 4100 - 4500 cm^{-1} region was recorded at Doppler - limited resolution and four bands were analysed: at lower wavenumbers, two strong bands, which, in the local mode picture, can be assigned to (200, E) (ν_0 = 4308.5670 cm^{-1}) and (200, A_1) (ν_0 = 4307.8439 cm^{-1}) , and at higher wavenumbers, two weaker bands, namely (110, E) at 4378.1950 cm^{-1} and (110, A_1) at 4375.9765 cm^{-1}. A total number of ca. 1900 lines in the strong dyad and 1000 lines in the weak one were assigned and fitted with standard deviations of the residuals $\approx$ 0.0007 cm^{-1}.

The strong system (200) is close to local mode behavior with almost no Coriolis effects (the $A\zeta_5^z$ term has decreased by a factor 35 from the ν_4 fundamental and changed sign), and simple arithmetic relations between vibration - rotation parameters are fulfilled as expected. The local mode behavior of the weak system (110) is less pronounced but z and x,y Coriolis effects are much smaller than in the Si - H stretching fundamentals.

HIGH-RESOLUTION FTIR SPECTRUM OF VINYL CHLORIDE
IN THE 680-1000 cm^{-1} REGION.

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The infrared spectrum of natural CH_2=CHCl has been recorded in the v_8, v_{10}, and v_{11} region (680-1000 cm^{-1}) at a resolution of about 0.005 cm^{-1} by means of a Bruker IFS 120 HR spectrometer.

CH_2=CHCl is a planar molecule belonging to the symmetry point group C_s and the vibrations of A' species (v_8) give rise to **a/b** hybrid bands, while those of A" symmetry (v_{10} and v_{11}) produce **c**-type envelopes. Since the asymmetry parameter κ is $\approx$ -0.98, this molecule approaches to a prolate symmetric top and the structure of the absorptions would correspond to that of parallel (**a**-type) and perpendicular (**b**-, **c**-type) bands.

The v_8 vibration, centered at about 720 cm^{-1}, approximately represents the C-Cl stretching mode and the expected hybrid band shows a predominant **a**-type component with the band centre region dominated by a series of $^Q Q_K(J)$ resolved sub-branches. The rovibrational analysis led to the identification of more than 2500 lines with $J \le 75$ and $K_a \le 13$.

At higher wavenumbers a binary system involving the v_{10} (~ 942 cm^{-1}) and v_{11} (~ 896 cm^{-1}) vibrations which approximately correspond to the CH_2 wagging and to the C=C twisting modes, respectively, gives rise to **c**-type profiles. The two bands overlap to a great extent, producing a quite crowded and irregular absorption pattern. Referring to the Q-branch characteristics, the J structure appears well resolved in most of the $^P Q_K$ and $^R Q_K$ sub-branches. The rovibrational analysis in the P, Q, and R branches led to an overall assignment of about 3000 transitions with $J \le 44$, $K_a \le 11$ for v_{10} and $J \le 58$, $K_a \le 12$ for v_{11}.

Employing the Watson's Hamiltonian in the I^r representation for the calculation of the energy levels, the identified lines allowed, for the three vibrations investigated, the determination of accurate upper state constants up to the quartic distortion terms that will be presented together with details of the spectrum and its interpretation.

THE DETECTION OF VERY WEAK ROTATION-VIBRATION-TRANSITIONS OF $D^{12}C^{14}N$ AND $D^{13}C^{15}N$ BY TUNABLE DIODE-LASER SPECTROSCOPY

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The rotation-vibration spectra of $D^{12}C^{14}N$ and $D^{13}C^{15}N$ have been recorded with a SPECTRA PHYSICS diode-laser spectrometer, consisting of a SP5800 laser source module, a SP5150 mode selector monochromator, and two MCT detectors.

Using a long path absorption cell, several very weak Q-branch transitions $02^{2f}0 - 00^00$ were observed for both isotopomers in the spectral region between $1\,123$ cm^{-1} and $1\,162$ cm^{-1}, with a signal to noise ratio of better than 10/1. These Q-branch transitions are forbidden, even when the effects of l-type resonance are taken into account, and therefore must be the result of some hitherto unknown Coriolis interactions[1]. Our diode-laser measurements supplement the FT-IR measurements of MAKI *et al.*[1]. Due to the weaker intensities of the transitions of the deuterated species and the inferior sensitivity of the FT-IR measurements, they obtained a satisfactory signal to noise ratio only for the hydrogen isotopomers.

Furthermore, the R-branch transitions of the $D^{12}C^{14}N$ isotopomer between the bending levels 060 and 040 were detected for all l substates for the first time. These transitions enabled us to determine spectroscopic constants for the previously uncharacterized 060 state.

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HOT BANDS IN THE REGIONS OF THE C-H AND C-C STRETCHING VIBRATIONS OF HCCI

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The hot band structures of the high resolution infrared spectra of monoiodoacetylene (HCCI) measured in the regions of the fundamentals v_1 (C-H stretch, 3265-3355 cm^{-1}) and v_2 (C-C stretch, 1990-2090 cm^{-1}) with instrumental resolutions of 0.0026 cm^{-1} and 0.0025 cm^{-1}, respectively, have been studied in detail. In addition, the weak overtone band $2v_2$ (4070-4130 cm^{-1}) has been recorded with a resolution of 0.0050 cm^{-1}. All the spectra were measured with a Bruker IFS 120 HR Fourier spectrometer in Oulu.

In the v_1 and v_2 regions rich hot band structures are observed and the measured spectra have been used to investigate the combination levels $v_1 = v_4 = 1$, $v_1 = v_5 = 1$, $v_2 = v_4 = 1$ and $v_2 = v_5 = 1$ as well as the overtone level $v_2 = 2$. Furthermore, three level systems $v_1 = v_3 = 1/v_1 = 1$, $v_5 = 2$, $v_2 = v_3 = 1/v_2 = 1$, $v_5 = 2$, and $v_1 = 1/v_2 = 1, v_4 = 2$ have been studied with models including ℓ- and Fermi-type resonances. As a result, the vibrational and rotational constants and the resonance parameters for the levels investigated have been obtained. These results together with former values[1,2] can be used to calculate the harmonic frequency ω_2^0 as well as the anharmonicity constants x_{22}^0, x_{23}^0, x_{24}^0, x_{25}^0, x_{13}^0, x_{14}^0, and x_{15}^0.

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HIGH RESOLUTION FTIR STUDY OF THE v_5 BANDS OF HSiD$_3$,
H^{70}GeD$_3$ AND H^{120}SnD$_3$

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High Resolution (0.0033 and 0.0028 cm^{-1}, respectively) infrared spectra
of HSiD$_3$ and monoisotopic H^{120}SnD$_3$ (admixed to ^{120}SnD$_4$) have been
recorded in the region of the isolated v_5 fundamentals located at 860.68
and 646.90 cm^{-1}. The analysis which employed the recently determined J-
dependent ground state parameters including $\Delta k = \pm 6$ interactions
responsible for the A$_1$A$_2$ splitting of the K = 3 ground state levels [1] was
performed with the concept of unitary equivalent reductions of the
rovibrational Hamiltonian according to Lobodenko et al.. More than 1500
lines of each species spanning J and K values up to 31 and 26 were
equivalently fitted with standard deviations of 0.11 and 0.14 x 10^{-3} cm^{-1},
respectively, to the two sets of excited state parameters with A-type
reduction (refining d$_5$) and with B-type reduction (refining r$_5$). The
previous analysis of the v_5 band of H^{70}GeD$_3$ [2] was extended and
improved. The K-dependent ground state parameters C$_0$ and D$_{K,0}$ of
HSiD$_3$ and H^{120}SnD$_3$ were determined for the first time, and "true"
parameters of the v_5 = 1 state of the three homologues have been
obtained.

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ELECTRONIC STATES OF SCANDIUM MONOIODIDE

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The many electronic transitions observed in high resolution spectra of the fluorescence of scandium monoiodide following excitation by Ar^+ and Kr^+ laser lines have been analysed. Equilibrium vibrational and rotational constants are obtained for the six lowest electronic states : $X^1\Sigma^+$, $a^3\Delta$, $b^3\Pi$, $A^1\Delta$, $c^3\Sigma^+$ and $B^1\Pi$. Spin-orbit constants in $a^3\Delta$ and $b^3\Pi$ are also determined. The laser-excited levels are regrouped into two electronic states of $^1\Pi$ and $^3\Pi$ symmetries, for which molecular constants are derived.

Moreover, the $B^1\Pi$ - $X^1\Sigma$ system which appears well developed in the thermal emission is studied extensively. Perturbational effects in the bands with v"=1 are analysed, being interpreted as a consequence of the avoided crossing between the levels $X^1\Sigma^+$ (v=1) and $a^3\Delta_1$ (v=0) at J = 70. At last, a faint system is ascribed to $C^1\Sigma^+$ - $X^1\Sigma^+$. Preliminary molecular constants for the $C^1\Sigma^+$ state are proposed.

SUB-DOPPLER STUDY OF THE ALLOWED AND $\Delta K= -3$ FORBIDDEN Q(3,3) TRANSITIONS TO THE ν_2 VIBRATIONAL STATE OF $^{14}NH_3$

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IR-IR double resonance and saturation sideband spectroscopy have been used to measure the allowed and $\Delta k = -3$ forbidden transitions to the ν_2 vibrational level of $^{14}NH_3$. This IR-IR double resonance experimental technique has made possible to observe quadrupole hyperfine structures which correspond to the sums as well as differences of the $^{-3}Q(3,3)$ and $Q(3,3)$ fine components. The „sum" and „difference" double resonance frequencies have been measured with accuracy under 30 kHz and 5 kHz, respectively. In addition to this, the hyperfine structure of the allowed $Q(3,3)$ transition has been independently measured using the „standard" saturation sideband spectroscopy with accuracy under 15 kHz. A simultaneous analysis of all measured data provides an improved set of effective nuclear quadrupole and spin-rotation parameters for the excited ν_2 vibrational state and, as the most important result, frequencies of the „pure" rotation-vibration transitions deperturbed from the hyperfine effects, including a very precise value of the „forbidden" spacing between the energies of the ν_2 $|J = 3, K = 3\rangle$ and $|J = 3, K = 0\rangle$ „pure" rotational levels of 2883.67989(61) MHz [0.096189207(21) cm^{-1}].

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PRESSURE BROADENING AND SHIFT OF CO_2 LINES AROUND 1.57 μm

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A distributed feed-back diode laser has been used for measuring pressure induced self broadening and shift for several transitions in the $v_1+2v_2+v_3$ band of CO_2 around 1.57 μm. Also foreign broadening and shift, with N_2 and O_2 as perturbing gas, have been measured for the most intense lines, allowing the estimate of air broadening and shift coefficients. To our knowledge these are the first lineshape measurements in this band and no comparison can be made with previous measurements. Nevertheless, at least for self and air broadening, a comparison can be made with the data given by the HITRAN database,[1] which assumes that broadening does not depend on the vibrational states involved in the transitions, and thus extends to all the other bands a least square polynomial fit of available experimental data, measured on a limited number of bands. The comparison shows in general a good agreement for self broadening, so comfirming the weak dependence of broadening on the vibrational quantum numbers, although for some values of the rotational quantum number J discepancies are observed; these discrepancies are more evident for air broadening coefficient. All the measured shift are negative as expected from theoretical models,[2] and a clear dependence on J has been observed. Moreover, the mean values, −0.56 MHz/Torr for self shift and −0.41 MHz/Torr for N_2 and O_2 shift, can be compared to the values found for other bands, giving an indication of the strong influence of vibrational quantum numbers on the shift, contrary to the case of broadening.

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LASER OPTOGALVANIC SPECTROSCOPY OF N_2 FROM THE $A^3\Sigma_u^+$ METASTABLE STATE IN A CORONA EXCITED SUPERSONIC EXPANSION

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A hollow cathode combined with a corona excited supersonic expansion was proven to be a very efficient method to produce a stable discharge in an N_2/Ar gas mixture. A high resolution and rotationally cold absorption spectrum of the well-known (2, 0) and (8, 7) bands of the $B^3\Pi_g \leftarrow A^3\Sigma_u^+$ first positive system of N_2 was recorded. It illustrates the sensitivity of the laser optogalvanic detection technique coupled to such an experimental set-up. A significant reduction of the linewidth and an enhancement of the signal to noise ratio were obtained. A high vibrational excitation process has been observed and is discussed [1].

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STRONG CORIOLIS COUPLING BETWEEN ν_5
AND ν_{11} STATES OF CH$_3$CCl$_3$
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We have recently completed the analysis of the mm-wave rotational spectra of the ^{37}Cl substituted species of 1,1,1-trichloroethylene.[1] In the course of that study we noted that, midway between successive J transitions of the common species, there are two extended symmetric top type bands characterised by J dependent, negative apparent D_{JK} of considerable magnitude, with values as low as -25 kHz. This was unusual in view of the large implied $B_v - B_o$ and the fact that in the ground state and in the lowest excited states ν_6 and ν_{12}, of CH$_3$CCl$_3$ $D_{JK} \approx$ -0.35 kHz.[2] Closer inspection of the spectra revealed the presence of an even more diffuse third set of bands much that for a given J, their effective D_{JK} was positive and close to the sum of the magnitudes of the values for the two remaining bands.

Ab initio calculations predicted the next higher, unassigned, pair of vibrational states, ν_5 of A-symmetry, and ν_{11} of E-symmetry to be only several cm^{-1} apart, at ca. 330 cm^{-1}. Analysis of the observed bands in the framework of Coriolis coupling was successful in fitting the observed patterns, resulting in $\Delta E = 2\ 403$ cm^{-1}, $\left|\zeta_{11}^{rc}\right| = 0.099$, $\left|\zeta_{5,11}^{a}\right| = 0.470$. These values are in good agreement with $\left|\zeta_{11}^{rc}\right| = 0.070$, $\left|\zeta_{5,11}^{a}\right| = 0.478$ from the 631G** *ab initio* force field. The proximity of the two states results in the dominant effect of the $\left|\zeta_{5,11}^{a}\right|$ in the Hamiltonian. The observed broadband spectra and the preliminary results of fitting over 600 transition frequencies measured in the region 120-340 Ghz are presented.

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THE ELECTRONIC STRUCTURE OF TiCl AND TiCl$^+$

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The electronic structures of the titanium chloride and its cation have
been analyzed by means of both ligand field (LFT) and density functional
(DFT) theories. From the general trends of the observed bonding distances of
the 3d-transition metal chlorides, the R_e value of TiCl has been deduced and
used as an input in the ligand field calculations on this radical. The
experimental assignement of the congested bands of TiCl observed between
3800 A and 4200 A, as well as the nature of the ground state, are very
controversed. In our calculations, both LFT and DFT have led to a $^4\Phi$ state
as the ground state for this molecule.

In the last time, a number of studies have focused on TiCl$^+$, the
electronic spectrum of which was investigated using different experimental
techniques[1,2]. The $^3\Phi$ assignement for the ground state of this molecule,
predicted by Kaledin et al.[3], using LFT calculations, was confirmed. Very
recently, Focsa et al.[4] analyzed a $\Delta\Omega=0$ transition involving the $[17.8]^3\Delta$
state leading to the identification of the A $^3\Delta$ state, which was found to lie at
550 cm^{-1}, i.e. 2000 cm^{-1} below the position predicted by Kaledin et al.[3].
This information have permitted to reinvestigate the spectrum of TiCl$^+$
yielding to new locations for most of the excited states.

Moreover, our results allow to understand the observed $X^3\Phi$ ground
state of the cation as resulting from a σ_s^{-1} ionization process of the TiCl
$X^4\Phi$ ground state. The ionization energy was calculated to be 7.31 eV.

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EMISSION SPECTROSCOPY OF THE UPPER ATMOSPHERE

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A cryogenic balloon-borne limb emission sounder based on the FTIR spectroscopy technique, known as MIPAS-B (Michelson Interferometer for Passive Atmospheric Sounding), has been developed and was used several times in co-ordinated field campaigns to measure a comprehensive set of stratospheric chemical compounds which are relevant for ozone chemistry and climate research. The instrument is specially tailored to the operation on a stratospheric balloon gondola and equipped with suitable subsystems to precisely allow limb emission sounding of the stratosphere independent of external radiation sources. The interferometer provides two-sided inter-ferograms with a maximum optical path difference of 15 cm resulting in an unapodised spectral resolution of 0.033 cm^{-1}. The four-channel detector system with Si:As BIB detectors allows the simultaneous coverage of the most important absorption bands of ozone- and climate-relevant molecules between 5 and 14 μm. A novel solution has been realised for the line-of-sight stabilisation and reference system. MIPAS-B is suitable to simul-taneously obtain vertical profiles of ozone and a considerable number of chemically coupled key radicals (NO, NO$_2$), reservoir species (HNO$_3$, HO$_2$NO$_2$, N$_2$O$_5$, ClONO$_2$, COF$_2$), and source gases (CH$_4$, N$_2$O, H$_2$O, HDO, CF$_2$Cl$_2$, CCl$_3$F, CHF$_2$Cl, CCl$_4$, CF$_4$, C$_2$H$_6$, and SF$_6$) with an altitude resolution of 2 - 3 km. A major benefit of the underlying measurement concept is its suitability for chemical process studies and for validation of satellite-based data. The talk will outline the experimental set-up, the methodology applied, and the scientific relevance of the data obtained with MIPAS-B. Special emphasis will be given to the importance of high-quality spectroscopic parameters for obtaining reliable retrievals of chemical constituent distributions.

HYPERFINE SRUCTURES IN THE ROTATIONAL SPECTRA OF MOLECULAR COMPLEXES

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The rotational spectrum of rigid molecules in the microwave and millimeter wave region is determined by three principal moments of inertia. If the molecule or molecular complex is nonrigid, the spectral lines are shifted due to centrifugal distortion and if additionally tunneling motions, e.g. internal rotation, inversion, or more complicated internal motions, are present, a tunneling fine structure is observed.

The rotational spectrum is also influenced by the interaction of nuclei having electric quadrupole moments which may interact with the electric field gradient caused by the electronic environment of the nuclei. The resulting nuclear quadrupole hyperfine structure therefore yields information on the properties of the chemical bonds. Nuclei with a magnetic dipole moment can interact with the magnetic field caused by the rotation molecule resulting in a magnetic hyperfine structure.

Since molecular beams are used in microwave spectroscopy the investigation of molecular complexes like van der Waals- or hydrogen bonded complexes, became available. In these systems the nature of the bond between the monomers is of special interest. If a quadrupolar nucleus is involved in such a bond, the coupling constants of the monomer and the complex may be compared. The difference between them reflects the electron transfer upon complexation. If quadrupole coupling constants are also available for the liquid phase, this will provide information on the contribution of hydrogen bonds in the liquid phase.

General theoretical and experimental aspects of nuclear quadrupole hyperfine structures in the rotational spectra of molecular complexes will be discussed and some results for special systems obtained from molecular beam Fourier transform microwave (MB-FTMW) spectroscopy will be presented.

K1

WIGNER STATISTIC OF THE NEAREST NEIGHBOUR DISTRIBUTION
OF HIGHLY VIBRATIONAL STATES OF CS_2.

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Experimentally, a Wigner statistic (chaotic dynamics) in the vibrational spectrum has been evidenced only in a few molecules like NO_2 or C_2H_2 . In CS_2, a transition to soft chaos has been evidenced [1]. Recently, we have performed new experiments of dispersed fluorescence spectroscopy at very high energy. 400 vibrational levels have been obtained in the range 19000-19600 cm^{-1}. This spectrum shows a complete wignerian statistic .

The situation is quite complex at these energies. In particular, there is no effective hamiltonian model. However, both the extrapolation of the low energy fitting hamiltonian and the comparison with the ab-initio potential of Chambaud and Rosmus [2] show that the experimental density of states around 19000 cm^{-1} is 3 or 4 times larger than the expected one. Several hypothesis are considered to explain this fact. We will present the evolution of the statistic with the density of states. We will then explain why the chaos was only soft at 19000 cm^{-1} in [1]. The question of the density of states is also of importance because we now have to understand which system is chaotic; is it a purely vibrational or a ro-vibrational chaos?

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K2

IR SPECTROSCOPIC STUDY OF THE VIBRATIONAL–ROTATIONAL SPECTRUM OF N_2O_3 AT 1830 cm^{-1}

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Using a continuous slit–jet expansion in combination with a computer controlled diode laser spectrometer, the vibrational–rotational spectrum of N_2O_3 has been studied.

The N_2O_3 molecule can be described as a quasi van der Waals complex formed between NO_2 and NO. Its binding energy (about 3344 cm^{-1}) lies just between that of a typical van der Waals molecule (Ar–NO: 88 cm^{-1}) and that of a typical chemical bond (NO: 52410 cm^{-1}). Till now, only two (ν_1 [1, 2] and ν_3 [3]) of its six vibrational bands are detected at high resolution.

In this work, 243 a-type infrared transitions of the ν_1 band (N–O stretch of N_2O_3) were measured at about 1830 cm^{-1} with a signal to noise ratio of 200:1 and fit with a standard deviation of 0.001 cm^{-1}. In addition, ground state rotational constants were calculated by fitting ground state combination differences together with microwave transitions [4].

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H_2O-Ar PROFILES IN THE MILLIMETER WAVE RANGE.
LINEWIDTHS, LINESHIFTS AND CONTINUUM

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With the use of a high Q Fabry-Perot interferometer, absolute absorption studies of water vapor with mixing gases are performed in the far wings of the H2O spectrum. In these atmospheric windows, the observed absorption shows large discrepancies with that obtained from the sum of impact profiles. As all the effects observed are not completely accounted for by the "continuums" derived by various authors, other collisional partners, such as the monoatomic gas Ar, have been chosen for a better understanding of the processes involved .

H_2O-Ar measurements have thus been carried out at 239 GHz. The observed absorption is compared to Van Vleck-Weisskopf models, where halfwidths of water vapor transitions in collision with argon are calculated using the Complex Robert-Bonamy Formalism (CRBF). Lineshifts are also calculated. The potential is a sum of electrostatic, atom-atom, induction, and dispersion components .The collision dynamics use the parabolic model of Robert and Bonamy. The calculated linewidths and -shifts are compared with previous values from infrared measurements.

The H2O-Ar continuum derived from these calculations is then compared with those obtained with N_2 and CO_2 collisional partners.

TRACE GAS DETECTION OF MOLECULES NEAR 3.5 μ USING LASER DIFFERENCE FREQUENCY GENERATION

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The development of a laser based real time room temperature sensor for detection of trace gases such as H_2CO, CH_4, and HCl is reported. The light source of the sensor is based on difference frequency mixing of a 1064.5 nm diode-pumped monolithic ring Nd:YAG laser and a tunable 815 nm GaAlAs diode laser in periodically poled lithium niobate ($LiNbO_3$), thus generating a tunable laser beam in the mid-infrared near 3.49 μ.

The present sensor is specifically configured to detect H_2CO. A minimum detection limit in the lower ppb-range of H_2CO is obtained at reduced pressure by performing direct absorption in a multipass cell with an 18 m pathlength.

A field instrument configured for monitoring of H_2CO based on this prototype is at the moment being build at Rice University.

MEASUREMENTS AND MODELLING OF THE LINE POSITIONS AND INTENSITIES FOR THE H_2S MOLECULE IN 4500 - 5500 CM^{-1} (FIRST HEXAD) REGION

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The Kitt Peak Fourier transform spectrometer was used to record H_2S spectra in 4500-5500 cm^{-1} region at 0.011 cm^{-1} resolution. More than 1400 precise experimental energy levels were derived after the spectrum identification for the first hexad ((100), (200), (002), (120), (021), (040)) of the resonating states of the $H_2^{32}S$, $H_2^{34}S$ species. The precise set of rotational constants was obtained from the fitting to the energy levels using Watson-type Hamiltonian, yielding RMS deviation of 0.001 cm^{-1}.

The transformed transition moment expansion coefficients were retrieved from the fitting to 1500 observed line intensities of the main isotope bands giving the RMS deviation of 3%. The strong link between energy levels and intensity fittings is found to take place. The second derivatives of the dipole moment with respect to normal coordinates were estimated and compared with existing ab initio values. The synthetic absorption spectrum of the H_2S molecule in the 4500 - 5500 cm^{-1} region is also presented.

SETTING OF A Ti:Sa SPECTROMETER

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We are setting up a spectrometer based on a COHERENT 899-29 Autoscan Ti:Sa laser connected to a White-type multiple pass absorption cell. Absorption path lengths over 100 m can be reached. We have tested the spectrometer by recording the $P(19)$ line of the 0-0 band of the $b^1\Sigma_g^+ - X^3\Sigma_g^-$ electronic transition in $^{16}O_2$ under various pressure conditions. We observed all the effects reported in the literature,[1,2] including Dicke type narrowing. New spectroscopic results will be presented in the range accessible, i.e. 12000-14000 cm^{-1}.

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DIAGNOSTIC AND MODELING OF N_2O HOLLOW CATHODE
DISCHARGES. TIME-RESOLVED FTIR EMISSION STUDIES.

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The hollow cathode discharge dissociation in N_2O has been studied
using continuous and modulated discharges and employing several diagnostic
techniques: FTIR absorption measurements have provided data for
determining the concentrations of N_2O and of the other infrared active
molecular species produced in the plasma (NO and NO_2); quadrupolar mass
spectrometry has allowed to estimate the O_2 and N_2 concentrations, and a
Langmuir probe has permitted the measurement of electron densities.

Some well stablished rate constants of the kinetic model have been
taken from the literature but, due to the important role played in our
discharge cell by surface combination and deactivation processes, additional
rate coefficients have been determined. The predictions of the model have
been also compared with the ones provided by the presently available models
for N_2O radio frequency (RF) discharges [1,2].

When using modulated discharges, time-resolved FTIR emission
spectra have been recorded with a Bruker IFS66 instrument, having a
maximum time resolution of 5 μs. The experimental data are compatible
with the model predictions.

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PRECISE LINE PARAMETERS AND CROSS-SECTIONS OF THE OXYGEN A BAND FOR $O^{16}O^{16}$ AND ITS ISOTOPOMER $O^{16}O^{18}$

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High-resolution Fourier transform absorption spectroscopy was used to investigate the visible $b\,^1\Sigma_g^+\,(\nu = 0) \leftarrow X\,^3\Sigma_g^-\,(\nu = 0)$ band ('A band') of molecular oxygen $O^{16}O^{16}$ and its isotopomer $O^{16}O^{18}$ to determine line parameters and cross-sections in order to improve the currently available data for application in atmospheric science. Spectra were recorded at room temperature, as well as at 198 K, covering pressures between 21 hPa and 1000 hPa, and pathlengths between 32 m and 128 m, with resolutions between $0.0069\,\mathrm{cm}^{-1}$ and $0.028\,\mathrm{cm}^{-1}$ depending on the density of the absorbing gas. A non-linear least-squares line-fitting procedure was applied in order to determine the individual line parameters in each of the spectra. Line intensities and self-broadening coefficients for $O^{16}O^{16}$ and $O^{16}O^{18}$ are presented. Using this data in an intensity analysis, the band intensity, the cross-section and the Einstein transition probability (A coefficient) of the A band were derived for both isotopomers, with accuracies of better than 1 % for $O^{16}O^{16}$ and better than 10 % for $O^{16}O^{18}$. Effects of different optical densities in the absorption experiment on the line-shapes, the line intensities and the cross-sections are investigated and discussed in comparison to previous results.

Integrated Band Intensities of Chloroform and Fluoroform.

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The infrared spectrum of two proposed replacements for chlorofluorocarbons Chloroform ($CHCl_3$) and Fluoroform (CHF_3) has been measured at a variety of pressures and temperatures using a Bomem DA3.002 Fourier transform spectrometer. These measurements were made as part of a joint programme to estimate the green house warming potential of such gasses[1]. These spectra have been used to calculate integrated band intensities for fluoroform in the regions $1100 - 1250cm^{-1}$ and $1330 - 1430cm^{-1}$ and for chloroform in the regions $740 - 800cm^{-1}$ and $1180 - 1240cm^{-1}$. A study of the ordinate errors in spectra produced by the spectrometer used for these measurements and their effect on integrated band intensities calculated from these spectra has been made and the integrated band intensities for fluoroform and chloroform have been corrected for these errors.

NLTE Effects in the NO Fundamental Bands

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A NLTE model of the $NO(1/2,1)$ and $N0(3/2,1)$ state populations is presented. Radiative transfer is treated using line-by-line computed transmittances. The impact of radiative and collisional processes and atmospheric parameters such as O_2- and O-distribution have been studied.

Resulting vibrational temperatures have been applied to line-by-line calculations under consideration of NLTE in order to simulate limb emission spectra in the 1870 cm^{-1} region of the NO fundamental bands. The impact of the NLTE effect on the limb radiance and the sensitivity of the spectra to the vibrational temperatures have been studied with regard to the retrieval problem.

K11

VECTOR AND SCALAR CORRELATIONS IN THE 193 nm
PHOTODISSOCIATION OF CH$_3$COCN

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High-resolution transient frequency modulation (FM) spectroscopy[1,2] has been used to measure nascent Doppler profiles of CN $\left(X^2\Sigma^+\right)$ fragments from the 193 nm photodissociation of acetyl cyanide (CH$_3$COCN). The determined global CN vibrational and rotational state distributions are in agreement with recent work[3]. The trends and magnitudes of the state-dependent translational energy distributions are inconsistent with statistical partitioning of the available energy. The CN fragments exhibit significant **v.j** corrrelations, indicating a preference for CN rotational angular momentum to be perpendicular to the relative velocity. These **v.j** correlations increase with detected CN rotational and vibrational quantum number state. No laboratory-frame alignment of CN velocity or angular momentum is observed. From a comparison of models for energy partitioning we conclude that the CN we observe arises primarily from C-CN bond cleavage over a modest exit barrier. The CN quantum yield suggests that the CN elimination competes with CH$_3$ elimination despite a large difference in C-C bond strengths.

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K12

LINE BROADENING IN THE ν_2 AND ν_5 BANDS
OF $^{12}CH_3F$ PERTURBED BY O_2.

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In previous works, we have determined the broadening coefficients in the ν_2 and ν_5 bands of $^{12}CH_3F$ using N_2 [1] and $^{12}CH_3F$ [2] as buffer gases. As a natural sequence of these studies, we report in this work O_2-broadening coefficients γ_0 in the same ν_2 and ν_5 bands of methyl fluoride.

The measurements were performed using our tunable diode-laser spectrometer [3]. More than forty absorption lines with J values ranging from 1 to 23, and K from 0 to 9 ($K \le J$) have been studied in the spectral range 1416-1573 cm^{-1}, which have been covered by one Pb-Sn-Te diode. Each of these lines was broadened by O_2 at pressures comprised between 10 and 55 mbar. The collisional widths have been obtained by fitting the Voigt and Rautian lineshapes to the line profiles.

Moreover, the broadening coefficients γ_0 of these lines have been calculated on the basis of the semi-classical model developed in Ref. [4] for the interaction between a symmetric-top and a non polar molecule. Comparisons between measured and calculated γ_0 values for the parallel ν_5 band as well as for the perpendicular ν_2 band are finally shown.

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LINE SHIFT IN FUNDAMENTAL BANDS
OF DIFFERENT ISOTOPOMERES
OF CARBON MONOXIDE

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We present in this paper results concerning line shift and line broadening in the fundamental band near 2058 cm^{-1} of five isotopomeres of carbon monoxide ($^{12}C^{16}O$, $^{13}C^{16}O$, $^{12}C^{18}O$, $^{13}C^{18}O$, and $^{13}C^{17}O$). The study includes collisions with N_2, O_2, H_2, D_2, He, Ne, Ar, Kr, and Xe. The line shifts of the isotopomeres $^{13}C^{16}O$, $^{12}C^{18}O$, $^{13}C^{18}O$, and $^{13}C^{17}O$ were studied for the first time. The results for Kr, H_2, and D_2 represent the first experimental data for the $(1\leftarrow0)$ band of CO at all. For all perturbers except helium all line-shift coefficients are negative. Within the experimental uncertainties the data show no significant dependence on the isotopomere. As known for $^{12}C^{16}O$ for collisions with noble gases the absolute value of the line-shift coefficients increase with increasing mass of the perturber. Lines from R-branches show smaller shift coefficients compared to P-branch lines. Our absolute values for the line-shift coefficients for the $(1\leftarrow0)$ band confirm the trend that the effect for this band is smaller compared to the $(2\leftarrow0)$ band as known from former experimental data by Bouanich *et al.*[1]. The nitrogen broadening will be compared to previous measurements for $^{13}C^{16}O$ by Voigt *et al.*[2].

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ON ISOTOPE EFFECT IN THE EXPANDED LOCAL MODE APPROACH: XY_2 (C_2V) MOLECULES

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Earlier[1, 2], "expanded" local mode method was derived, which allows one to considerably move apart frameworks of efficient in chemical physics local mode approach.

In present paper this method is further derived, and influence of isotope substitutions of light atoms on properties of Hamiltonians, spectroscopic parameters, etc., of different isotopic species is considered. It is shown that analysis of properties of transformation coefficients allows one to obtain sets of new nontrivial (and, at the same time, simple) relations between harmonic ϖ_λ, anharmonic $\chi_{\lambda\mu}$, vibrational-rotational α^β_λ, centrifugal distortion, resonance interaction parameters of different isotropic species.

XY_2 $(C_2V$ symmetry) molecules are considered as an example. For illustration, numerical calculations on the base of obtained general relations are made for the H_2S - HDS - D_2S species, and results are compared with experimental data.

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K15

USE OF QUANTUM-MECHANICAL CALCULATIONS AND
ROTATIONAL ANALYSIS TO DETERMINE THE STRUCTURE OF
THE HIGH ENERGY CONFORMER OF 1,3-BUTADIENE

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The force fields of the planar *trans* and *cis* forms and the non-planar *gauche* form of 1,3-butadiene (I) are calculated at the MP2/6-31G //MP2/6-31G level. The scale factors for the quantum-mechanical force field of the *trans* conformer are determined from the experimental vibrational frequencies of its light isotopomer. The scale factors obtained are transferred to the quantum-mechanical force fields of the *cis* and *gauche* forms. The corresponding vibrational problems are solved. A special region of the IR spectrum of I ($710 \div 790$ cm^{-1}) is determined in which only a band attributable to the *gauche* rotamer should be present. Investigation of the medium and high resolution IR spectra of I in the gas phase revealed the presence of a band at 749.22 (20) cm^{-1} possessing a typical B contour [1]. Rotational analysis of the medium resolution spectrum of this band yields the rotational constants $(A' - \widetilde{B}') = 0.4455$ (25) cm^{-1} and $(A'' - \widetilde{B}'') = 0.4478$ (27) cm^{-1}. They are rather close to the value determined from the quantum-mechanical parameters of the *gauche* conformer as scaled using the corresponding quantum-mechanical results and the experimental data on the *trans* conformer. The extremely complicated character of the high resolution spectrum of this band also suggests that geometry of the high energy conformer of I in the gas phase is non-planar *gauche*.

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ANHARMONIC COUPLING IN THE OVERTONE

SPECTRA OF CH_3F, CHD_2Cl, CH_2D_2 AND C_2D_4

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The harmonically coupled anharmonic oscillator model of overtone vibrations is systematically extended to include local mode *anharmonic* coupling terms. Quantitative relationships between the parameters of this improved local mode model and those of the normal mode approach are derived. Applications are made to the overtone spectra of CH_3F, CHD_2Cl, CH_2D_2 and C_2D_4 (allene) and various hitherto anomalous observations rationalised by analysis of previously neglected anharmonic effects. Fermi resonance coupling between C–H (or C–D) stretching and bending states is important is the first three systems listed above; incorporation of such effects into the model is readily achieved.

THEORETICAL PREDICTION OF VIBRATIONAL
STATES FROM ANHARMONIC FORCE FIELDS

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Different aspects of the *ab initio* determination and utilization of anharmonic molecular force fields, expressed as a Taylor series expansion of the potential energy up to sixth order, are presented. Accuracy of *ab initio* quartic and sextic force fields is addressed,[1,2] as well as pertinent issues related to choice of the reference geometry,[1] basis set, and level of electron-correlation treatment.[1,3] A simple and compact method[4] is described which enables determination of general derivative relations for anharmonic force fields.

Problems associated with the derivation of vibrational kinetic energy operators in internal coordinates are discussed. Twenty analytic expressions,[5] the maximum number of distinct terms occuring in any given vibrational kinetic energy operator of N-atomic sequentially bonded molecules, are given which are applicable if the valence stretch, bend, and torsional coordinates are chosen to describe the dynamics of the molecule.

A quartic force field of water, determined at the aug-cc-pVQZ CCSD(T) level of theory, has been employed in a perturbation-resonance approach[6] to calculate the high-lying vibrational levels of water up to 12 000 cm^{-1} above the zero-point level. The accuracy of the directly determined levels is impressive and could further be improved with a predicated least-squares refinement of the quartic force field.

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AB INITIO CALCULATIONS FOR CYANOPOLYYNES HC$_{2n+1}$N AND THEIR PROTONATED SPECIES

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Large-scale coupled cluster calculations including connected triple substitutions have been carried out for cyanopolyynes and their cations up to HC$_9$N/HC$_9$N$^+$. Accurate equilibrium geometries are established. The ground-state dipole moments of HC$_7$N and HC$_9$N are predicted to be -4.82 and -5.20 D, with an estimated uncertainty of 0.02 D.

The equilibrium rotational constants for HC$_5$NH$^+$ and HC$_7$NH$^+$ are 1294.1 and 553.2 MHz; they should also be good estimates for the ground-state values. The electric dipole moments of the cations, evaluated in the center-of-mass coordinate system, increase strongly with lengthening of the carbon chains. We predict μ_e (HC$_5$NH$^+$) = 3.81 D and μ_e (HC$_7$NH$^+$) = 6.35 D.

PHOTOIONIZATION EFFICIENCY SPECTROSCOPY OF TiO, YO, ZrO AND MoO

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The adiabatic ionization potentials of TiO, YO, ZrO and MoO have been measured using two-color photoionization efficiency spectroscpy. For TiO, single rotational levels of the $B^3\Pi_1$ (v = 0) state were used as intermediate levels. Rydberg progressions converging to the $X^2\Delta_{3/2}$ (v = 0)state of TiO^+ were observed but are overlapped by one-color two-photon transitions excited by the ionization laser. Nevertheless. the ionization potential has been determined to be 54995 ± 5 cm^{-1}. For YO, single rotational levels of the $A^2\Pi_{1/2}$ (v = 0) state were used as intermediate levels. Rydberg progressions converging to the J = 5-13 levels of the $X^1\Sigma^+$ state of YO^+ were recorded and fitted. The B value and the J = 0 level of the $X^1\Sigma^+$ (v = 0) state of YO^+ were determined to be 0.4094 ± 0.0004 cm^{-1} and at 49304.1 ± 0.1 cm^{-1}, respectively. For ZrO, single rotational lines of the $C^1\Sigma^+$ (v = 0) and $a^3\Pi_1$ (v = 0) were used as intermediate levels. Strong transitions excited by the ionization lasers prevented the observation of Rydberg progressions. However, mass-analyzed threshold ionization spectroscopy lead to a value of 54950 ± 15 cm^{-1} for the ionization potential. For MoO, levels of the $B'^5\Pi_{-1}$ (v = 0) state were used as intermediate level. No Rydberg progression converging to the $X^4\Sigma^-$ state of MoO^+ was observed. Nevertheless, the ionization potential was determined to be 60080 ± 10 cm^{-1}. The second -order spin-orbit separation in the $X^4\Sigma^-$ state of MoO^+ was determined to be 264 ± 20 cm^{-1}.

K20

EXPERIMENTAL INVESTIGATION OF LONG-RANGE
INTERACTIONS IN Na$_2$

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We report on detailed studies of the asymptotic level structure of the $A^1\Sigma_u^+$-state of Na$_2$ up to 100 MHz below the dissociation limit. A simple adiabatic model can describe these observations for low J and an extension including rotational coupling within the hyperfine levels agrees with the observations up to J=40 [1].

In addition we investigated Zeeman measurements of such asymptotic levels, the behavior of which is very unusual. We see only little influence of polarisation and rotation, but large linear and quadratic effects indicating strong electronic coupling.

Finally, we present an experimental scheme using coherent processes to investigate asymptotic levels of the ground state or of highly excited electronic states, which gives access to different kinds of long-range interactions.

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BOUND-BOUND AND BOUND-FREE A-X TRANSITION OF NO-Ar VAN der WAALS MOLECULE STUDIED BY LASER INDUCED FLUORESCENCE - PRELIMINARY THEORETICAL CALCULATIONS

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The lowest excited electronic states of NO-Ar associated with the $3s\sigma$, $A^2\Sigma^+$, $3p\pi$, $C^2\Pi$ and $3p\sigma$, $D^2\Sigma^+$ Rydberg states of NO, have been observed experimentally either by Laser Induced Fluorescence (LIF)[1] or by Resonant Multiphoton Ionization (REMPI)[2-4]. These states present an interesting situation in which the radius of the classical Rydberg orbit of the NO compound is of the order of magnitude of the intermolecular distance of the complex. The Ar-NO(A) state shows indeed a structure very different from that expected for a Rydberg state of Ar-NO. A strong continuum in the blue side of the pure NO A-X transition, associated to the repulsive part of the A state potential energy surface first observed by LIF[1]. Later on, mass resolved REMPI studies [2,3] concluded to a slightly bound state at very large intermolecular distance. In the present work, we have observed the fluorescence excitation spectrum of the A-X system in both regions, leading to a strong continuum band and, in the red side of it, to a weak bound structure consisting of 5 vibrational bands.

Ab initio calculations on the 3s and 3p states are presently under progress. They predict an important mixing between the 3 states of A' symmetry. Furthermore, the A state potential energy surface exhibits a very large anisotropy and an equilibrium geometry very different from the almost T-shape ground state and excited C and D states.

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K22

TIME DEPENDANT QUANTUM DEFECT THEORY
AUTO-IONISATION AND PRE-DISSOCIATION DYNAMICS

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inelastic stationary scattering theory including bound states. Temporal developments are quite recent: H.H.Fielding[1][2] and F.Robicheaux[3].

A phase-amplitude treatment is used to develop Time Dependent Quantum Defect Theory (TDQDT) for arbitrary long range potentials. Jungen and Ross[4] approach of ionization and dissociation in competition is used to calculate time dependent wave functions representing of hydrogen molecule excited by Gaussian pulse of arbitrary length. Wavepackets at different times, flux at different radii and delays are presented.

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Unified quantum-defect-theory treatment of molecular ionisation and dissociation

THE MICROWAVE SPECTRUM OF
4,5-DIMETHYLTHIAZOLE

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Using a molecular beam Fourier transform microwave spectrometer we measured and assigned the rotational spectrum of 4,5-dimethylthiazole in its vibronic ground state.

A rather complex fine structur of the rotational lines could be resolved. Due to two unequal internal methyl rotors each rotational line is split into five torsional components. Each component shows a hyperfine splitting caused by ^{14}N-quadrupole coupling.

The hindering potentials of the two internal rotors and the ^{14}N-quadrupole coupling constants will be compared with those obtained for 4-methylthiazole [1] and 5-methylthiazole [2] in previous studies.

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Rotational Spectrum of Isoxazole–CO

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Unlike noble gas atoms carbon monoxide has a small permanent electric dipole moment which may account for the widely different structures of the observed CO van der Waals complexes. For example, CO is found to interact with the π–electron system in pyrrole, furan and benzene — forming nonplanar complexes with CO above the ring plane — but in the case of pyridine CO unexpectedly preferentially interacts with the nitrogen lone pair of electrons resulting a planar complex.

Isoxazole — essentially furan with a pyridine-like nitrogen atom adjacent to the oxygen atom — can offer the CO molecule both π–electrons (as in furan) and a nitrogen lone pair of electrons (as in pyridine), and is thus a good candidate molecule with which to investigate the relative strengths of the two types of intermolecular interactions so far observed between CO and aromatic molecules. To this end the rotational spectrum of isoxazole–CO has been measured using a pulsed–jet Fourier transform cavity microwave spectrometer in the frequency range 6–18 GHz.

It is clear from the derived rotational constants that the complex is planar, and both the ^{14}N nuclear quadrupole coupling constants and electric dipole moment components show that the CO molecule is located between the nitrogen and oxygen atoms of isoxazole.

Hence, for both pyridine and isoxazole it appears that the nitrogen lone pair of electrons could be the dominant influence in the formation van der waals complexes with small polar molecules.

K25

MW Spectra and Internal Rotation of 1-4-difluoro-2-butyne and two Deuterated Species.

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The MW-spectra of the parent molecule of 1-4-difluoro-2-butyne ($CH_2F-C\equiv C-CH_2F$) have been investigated by A. Karlsson el al (1), who assigned the ground state and the first torsionally excited state. The spectrum in the ground state was a normal rigid rotor spectrum whereas a slight splitting of the lines in the excited state was attributed to internal rotation. In the present work the MW-spectra of the deuterated molecules, 1-4-difluoro-2-butyne-1-d_2 ($CH_2F-C\equiv C-CD_2F$) 1-4-difluoro-2-butyne-d_4 ($CD_2F-C\equiv C-CD_2F$), have been studied in the ground state and in the two lowest torsionally excited states and it is attempted to determine a potential function common to all three molecules.

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Rotational Spectrum of Vinylarsine

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We have studied for some years molecules with heavy atoms, bearing a double bond in α of the heteroatom. We present here the last results we obtained for vinylarsine $CH2=CHAsH_2$.

The assignment of its rotational spectrum was made using a Stark spectrometer in Valladolid. Higher-J transitions were measured in Lille.

Vinylarsine is composed of two conformers : a *syn* form with a plane of symmetry bissecting the -AsH$_2$ group, and a *gauche* form, as expected from *ab initio* calculations. The *gauche* form should be less stable than the *syn* form, but by only a few kJ.mol^{-1}.

In order to improve the values of the quadrupole tensor elements, we recently used in Lille a supersonic jet spectrometer to measure the quadrupole components of the $^aR_{0,1}$ $J = 1\leftarrow0$ and $J = 2\leftarrow1$ transitions at 7600 and 15000 MHz.

While vinylarsine is composed of two conformers, it was impossible to detect the lines of the *gauche* form.

For the *syn* form, all measured components from 7500 to 320000 MHz were included in a fit performed with the Pickett's program[1]. The diagonal elements of the quadrupole tensor, as well as two spin-rotation interaction constants, C_a and C_b, could be determined.

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ROTATIONAL SPECTRA OF NeH$^+$ AND NeD$^+$

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Rotational spectra of protonated rare gases have been observed with high-precision far-infrared spectrometers using tunable radiation sources for ArH$^+$ [1], HeH$^+$ [2], and KrH$^+$ [3]. By using this technique, we observed rotational transitions of ^{20}NeH$^+$ and ^{20}NeD$^+$ in their ground vibrational states.

The spectrometer used has been already described [4,5]. The sample cell is a liquid-nitrogen cooled discharge cell of 1.4 m length. A gas mixture of Ne:H$_2$ (or D$_2$) with a total pressure of $\sim$50 Pa and a typical mixing ratio of 40:1 was used for ac discharge. Transitions for J+1 $\leftarrow$ J with J $= 0 \sim 4$ for NeH$^+$ and those with J $= 2 \sim 8$ for NeD$^+$ have been observed in the 1 $\sim$ 5 THz frequency region with an accuracy better than 0.15 MHz.

Observed frequencies were analyzed together with vibration-rotation transitions observed by infrared spectroscopy [6,7]. Rotational and centrifugal distortion constants were determined for either isotopic species. A simultaneous fit of all the isotopic data was made to refine Dunham coefficients $Y_{k\ell}$ and isotopically independent parameters $\Delta_{k\ell}^{Ne}$ and $\Delta_{k\ell}^{H}$ determined in Ref.(5).

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FREE JET ABSORPTION MILLIMETER WAVE SPECTRUM OF THE HYDROGEN BONDED COMPLEX PYRAZINE-H_2O

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The free jet millimeter wave spectra of the hydrogen bonded complex pyrazine-H_2O and its mono and bi- deuterated isotopomers were investigated in the frequency range 60-78 GHz. The near prolate rotor spectra consisted of μ_b-type rotational transition, each of them split in two component lines of approximately equal intensity and with a statistical weight of 5:3 depending on the parity of K_a. The geometrical structure which is consistent with one water hydrogen bound to one pyrazine nitrogen, and with the oxygen lying in the plane of the aromatic molecule.

STUDY OF THE SPECTRA OF SILANE IN THE $3000cm^{-1}$ REGION BY FOURIER TRANSFORM SPECTROMETER

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Three Fourier Transform Infrared Spectra of SiH_4 has been recorded between 2930 and $3300cm^{-1}$ with the resolution of $1.8 \times 10^{-3}cm^{-1}$ and the following experimental conditions

- $T = 209K$; $p = 0.2torr$; $l = 12m$

- $T = 297K$; $p = 0.2torr$; $l = 20m$

- $T = 297K$; $p = 0.8torr$; $l = 20m$

The polyad $\nu_1+\nu_2(E)$, $\nu_1+\nu_4(F_2)$, $\nu_2+\nu_4(F_1+F_2)$ and $\nu_3+\nu_4(A_1+E+F_1+F_2)$ using the results of fundamental bending dyad ν_2, ν_4 [1] and the stretching dyad ν_1, ν_3 [2] and the vibrational extrapolation method have been studied. The comparison between the $297K$ and the $209K$ spectra gives some important informations on the Ground State of the transition. Some assignments of experimental transitions of each bands are made. This study, in progress, will be presented at the colloquium.

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Sensitive Overtone Spectroscopy of $2\nu_1$ of Chloroform ($CHCl_3$) with very High Resolution

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The overtone spectra of the CH chromophore in $CHCl_3$ have been of interest for some time in relation to femtosecond intramolecular vibrational redistribution and to the electric dipole function and band strengths [1–3]. The present paper aims at a very high resolution analysis of $2\nu_1$. Optothermal detection of the $2\nu_1$ (symmetric stretch) overtone transition of $CHCl_3$ molecules in a collimated molecular beam at $\lambda = 1.68\mu m$ excited by a single mode NaCl-colour center laser allows a Doppler-free spectral resolution of 5MHz. The rotational structure and the K-substructure of the two isotopomers $CH^{35}Cl_3$ and $CH^{35}Cl_2^{37}Cl$ could be resolved. While the Q-branches can be only resolved with sub-Doppler resolution, parts of the rotational structure of the P- and R-branch were also measured with Fourier spectrometers (Bruker and Bomen), as well as with OSVADPI laser technique. Analysis of the asymmetric rotor spectrum of $CH^{35}Cl_2^{37}Cl$ is in progress in the $2\nu_1$ vibrational state. The analysis of the symmetric top $CH^{35}Cl_3$ isotopomer meets serious difficulties because of severe perturbations.

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K31

THE ν_1 AND ν_{22} BANDS IN PYRROLE

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We have recorded the infrared absorption spectrum of pyrrole at 0.005 cm^{-1} spectral resolution using a Fourier transform interferometer. The rotational analysis of the fundamental N-H stretch (1_0^1) at 3530.811343 (82) cm^{-1} and of the fundamental out of-plane C-H bend (24_0^1) at 722.133134 (47) cm^{-1} were performed. Upper state rovibrational parameters were determined. The role of hot bands is investigated along the series of the N-H stretch excitation. Effective vibrational parameters $-\omega_1^0$, X_{11}^0, Y_{111}, $X_{1,24}$ $-$ are obtained. The lower level in the hot band series is unambiguously identified as the $\nu_{24} = 1$ level, by inferring $X_{1,24}$ independently from the spectral data.

K32

THE ROVIBRATIONAL ENERGY LEVELS IN ACETYLENE $^{12}C_2D_2$

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We perform the rovibrational analysis of the absorption spectrum of $^{12}C_2D_2$ between 5000 and 8000 cm^{-1}, recorded by Fourier transform spectroscopy, and between 13500 and 17500 cm^{-1}, recorded by Intracavity Laser Absorption Spectroscopy. Improved or new rovibrational parameters are obtained for several vibrational levels. We consider all known vibrational energies in $^{12}C_2D_2$ ($X^1\Sigma_g^+$) using a model combining a Dunham expansion with few anharmonic resonances. Vibrational parameters are inferred.

K33

HIGH-RESOLUTION STUDY OF THE FIRST STRETCHING OVERTONES OF $H_3Si^{79}Br$

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The Fourier transform infrared spectrum of monoisotopic $H_3Si^{79}Br$ has been studied from 4200 to 4520 cm^{-1}, in the region of the first overtones of the Si-H stretching vibrations. The aim of the present study is to estimate how close are these overtones from the local mode limit.

The investigation of the spectrum revealed the presence of a strong system comprising one parallel band (v_0=4340.2002 cm^{-1}) and one perpendicular band (v_0=4342.1432 cm^{-1}) and of a weaker perpendicular band, centered at 4418 cm^{-1}. The two stronger bands were identified as (200, A/E), and the weaker one as (110, E), in the local mode notation.

The rovibrational analysis revealed strong local perturbations for both the strong and the weak systems. 1135 transitions belonging to the strong system were fitted to a simple model involving a perpendicular component interacting by a weak Coriolis resonance with a parallel component. The most severely perturbed transitions, whose |obs-calc| values exceeded 2×10^{-3} cm^{-1}, were given zero weights in the fit. The standard deviations of the fit were 1.4×10^{-3} cm^{-1} and 0.77×10^{-3} cm^{-1} for the parallel and the perpendicular components of the (200) system, respectively. The rovibrational analysis showed that the vibrational energy is not yet completely localized, probably due to the great number of levels interacting with the v=2 levels.

Work is still in progress in order to identify transitions belonging to the weak parallel (110, A) band.

ABSOLUTE LINE INTENSITIES IN THE $2v_3$ BAND OF $^{16}O^{12}C^{32}S$

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The strengths of 100 lines in the $2v_3$ band of $^{16}O^{12}C^{32}S$ have been measured at high resolution in the spectral range 4069-4118 cm^{-1}, using a tunable difference-frequency laser spectrometer. These intensities were obtained by fitting Voigt profiles to the measured shapes of the lines. The vibrational transition moment [$(2.141 \pm 0.020) \times 10^{-2}$ D] and the absolute intensity (16.19 ± 0.24 cm^{-2} atm^{-1} at 296 K) of the $2v_3$ band of $^{16}O^{12}C^{32}S$ are determined from these line strength measurements.

HIGH-RESOLUTION FTIR STUDY OF THE $v_3 + v_4$, $v_1 + v_4$ AND $v_1 + v_2$ ROVIBRATIONAL BANDS OF **PF₃** BETWEEN 1100 AND 1500 cm⁻¹

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In 1995, H19 communication of the 14th. colloquium, which dealt with the same topic, gave only first assignments and rough preliminary fits with a special resolution of 4.4×10^{-3} cm⁻¹ [1]. Now, we have just finished the whole interpretation which leads to infinite chains in the final least squares calculations. 3600 IR transitions belonging to the ($v_3 + v_4$, $v_1 + v_4$) system and the 4 available MW transitions were fitted altogether with a model taking into account the ℓ (2,2) interaction inside $v_1 + v_4$ (E) and between $A_1 + A_2$ and E components of $v_3 + v_4$, the ℓ vibrational resonance inside $v_3 + v_4$ (A1 + A2) and the Coriolis resonance between $v_1 + v_4$ and $v_3 + v_4$ ($A_1 - A_2$) on the one hand and $v_3 + v_4$ (E) on the other. A r.m.s. deviation of 0.76×10^{-3} cm⁻¹ was obtained with 34 free parameters among 38. As for $v_1 + v_2$ (A1), 1815 transitions were fitted through a model taking into account the Coriolis interaction with the $v_2 + v_3$ (E) dark band, most of whose parameters were held fixed to the expected values. A r.m.s deviation of 0.55×10^{-3} cm⁻¹ was obtained with only 7 free parameters among 21. The Fermi resonance, which links $v_3^{\pm 1}$ to $v_2 + v_4^{\pm 1}$ with a coupling term $W_{234} = 2,86$ cm⁻¹ [2], must connect each component of $v_3 + v_4$ with each component of $v_2 + 2v_4$ and $v_2 + v_3^{\pm 1}$ with $2v_2 + v_4^{\pm 1}$. But, since we have little if any experimental information about these last bands, it was not possible to introduce this resonance in the fits. However, the band centre shifts were reached and the very sensitive anharmonicity constants x_{34} and g_{34} were deduced even if the x_{23} wasn't as accurate. Of course, the Fermi-independent x_{14} and x_{12} constants were the best.

[1]   The authors warmly thank Pr. H. Bürger from the Bergische Universität of Wuppertal (Germany) for synthesising the sample and recorded on his 120HR Bruker interferomete thespectrum which was used.
[2]   N. Ben Sari-Zizi, H. Bürger, M. Litz, H. Najib and J Radtke J. Mol. Spectrosc. 177, 46-57 (1966), article No 0116

K36

THE LOWEST INFRARED BANDS OF CS_2 WITH A RESOLUTION OF 0.001 CM^{-1} FOR CALIBRATION PURPOSES

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The first part of this series of investigations on the infrared spectrum of CS_2 consisted of the measurements of the weak $\nu_1+\nu_2$ and $3\nu_2$ bands above 1000 cm^{-1}. These spectra were calibrated with the aid of CO_2 laser lines. The results have been published[1].

The second part included the measurements of the difference band $\nu_1-\nu_2$ (262 cm^{-1}) and the lowest fundamental band ν_2 (396 cm^{-1}), both with many accompanying hot bands. The former region was measured in Lund (Sweden) with the aid of a synchrotron radiation source, the latter in Oulu. As a detector a liquid-helium-cooled bolometer was used in both Fourier spectrometers. The experimental line widths were 0.0010 and 0.0011 cm^{-1}, respectively. More than 2000 lines were assigned. In the polynomial fit of 115 lines from the ν_2 band the std. dev. was 8×10^{-6} cm^{-1}.

In the third part of the study the ν_2 region was calibrated by adding the lines from ν_2, $2\nu_2 - \nu_2$ and $3\nu_2 - 2\nu_2$ bands and by comparing the sums with the lines in the $3\nu_2$ band. Then in a corresponding way the $\nu_1-\nu_2$ region was calibrated against $\nu_1+\nu_2$ by making use of the bands ν_2, $\nu_1-\nu_2$, $\nu_1+\nu_2-\nu_1$, $2\nu_2 - \nu_2$ and $\nu_1+\nu_2 - 2\nu_2$.

[1] T.Ahonen, S. Alanko, V-M. Horneman, M. Koivusaari, R.Paso, A-M. Tolonen, and R.Anttila, J. Mol. Spectrosc. 181, 279 (1997).

K37

GLOBAL FITTING OF CO$_2$ VIBRATIONAL-ROTATIONAL LINE INTENSITIES USING THE EFFECTIVE OPERATOR APPROACH

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The effective operator approach is applied to the calculation of line intensities of $^{12}C^{16}O_2$. The experimental intensities of the cold and hot bands lying in the same frequency region have been fitted simultaneously to parameters of the corresponding effective dipole moment matrix elements. The eigenfunctions of an improved effective Hamiltonian, expanded up to sixth order in the Amat-Nielsen ordering scheme and the parameters of which have been determined by fitting all available vibrational-rotational lines, have been used. The regions of the v_2, $3v_2$, $5v_2$, $7v_2$, $9v_2$, $11v_2$ and $13v_2$ bands have been studied. The quality of the fittings and the extrapolational properties of the fitted parameters are discussed. The predictive power of the fitted parameters is illustrated on several examples, among which the forbidden $3v_2^3$ band. A comparison of the fitted parameters and the corresponding calculated ones from known force field and dipole moment derivatives is given.

K38

A STABILISED SCANNING HIGH RESOLUTION NIR DIODE LASER
SPECTROMETER

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We have previously developed a computer controlled
frequency modulated diode laser spectrometer capable of taking
high sensitivity spectral scans in the range 12670-12770 cm^{-1} and
tested its performance on water and other species active in this
band [1]. The reproducibility of frequency measurement in each
scan has been shown to be limited to 0.003 cm^{-1} by the thermal
stability conferred by our system on the diode source. By locking
the diode frequency to the zero crossing of the first derivative on a
piezo-controlled Fabry-Perot étalon peak, we have successfully
improved the precision of our measurements to 0.0003 cm^{-1}, well
below the spectral Doppler width. Some examples of high
resolution spectra taken using this technique are displayed.

[1] T D Bevis, J G Baker and N J Bowring, Poster K15, XIIII
Mol. Spec. Colloquium, Dijon 1995

Investigation of Structural Conformers In 4-Pyrrolidinobenzonitrile and Ethyl 4-Pyrrolidinobenzoate and their Clusters with Water and Argon.

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Laser induced fluorescence of the $S_1 \leftarrow S_0$ electronic transitions in 4-pyrrolidinobenzonitrile and ethyl 4-pyrrolidinobenzoate, and their clusters with water and argon (n=1,2), have been recorded in a jet cooled environment. Analysis of their their fully, or partially resolved rotational spectra, has provided insight into their equilibrium structures as well as their state-selected photophysics.

For 4-pyrrolidinobenzonitrile the fully resolved spectrum has been obtained and absolute transition frequencies determined to ± 8 MHz. This has allowed a fit using a general purpose rigid rotor program and unambiguous assignment of the structure.

In the case of ethyl 4-pyrrolidinobenzoate and and the seperately identifiable vdW complexes with argon and water, which have also been recorded and assigned, single line resolution was not achievable, however spectral simulations have allowed us to address some questions concerning the geometrical structures of the isolated host molecules and their microsolvated clusters.

This works extends a previous study carried out at low resolution[1] and gives new information on the geometrical structures accessible for these systems in a jet-cooled environment

[1]   Laser induced fluorescence spectroscopy and structure of micro-solvated molecular clusters.
B. D. Howells, J. McCombie, T. F. Palmer, J. P. Simons and A. Walters,
J. Chem. Soc. Faraday Trans., **88**, (1992) 2587, 2595 and 2603

L1

Tracking the Dynamics from Spectroscopic Excitation to Photo-dissociation

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The primary influence on the outcome of a molecular photodissociation is the nature of the potential energy surfaces involved and of any coupling between them. In predissociation the lifetimes of the transiently excited states are also important, such that different excited levels can result in different populations of product states, or even different products. In some cases this product distribution may be entirely statistical in nature, but in others be dynamically controlled. This paper will review some of the experimental and theoretical techniques used to measure and interpret current studies in our group. The various mechanisms will be illustrated with reference to parent molecules such as methane, ammonia, methylamine and formyl fluoride. In ammonia the dissociation from the structured $\tilde{A}$ state is almost entirely dynamically controlled for NH_3. Deuteration increases the extent of statistical rotational energy distribution in the NH_2, NHD or ND_2 products, but the most statistical case is not for ND_3. The dissociation of formyl fluoride through its long-lived $\tilde{A}$ state yields mainly H atoms and FCO radicals in which the rotational energy is dynamically determined but the vibrational energy release is statistical. These differing outcomes will be shown to derive from the properties of the potential energy surfaces well removed from those of the initially excited states.

L2

PHOTOASSOCIATION BELOW 1 mK:

A NEW LIGHT ON MOLECULAR SPECTROSCOPY

P. D. Lett

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Ultracold photoassociation spectroscopy[1] is the formation of bound, excited, diatomic molecules by the absorption of a photon during the collision of trapped, laser-cooled atoms. While photoassociation is not new, the extremely low energy of the colliding atoms (< 1mK) in this case gives the technique a number of unique and desirable properties. The resolution obtained for such free-bound electronic transitions is < 0.001 cm^{-1} and the technique favors transitions to molecular states very close to dissociation which are traditionally difficult to access in bound-bound spectroscopy.

One of the unique capabilities demonstrated by this technique has been the spectroscopy of "purely long range" states of the alkali dimers. In Na_2, for instance, the 0_g- potential dissociating to $S + P_{3/2}$ is only 2cm^{-1} deep and has *inner* turning points near 55 a_0. Two-color spectroscopies[2], either to doubly-excited states or to the uppermost bound states of the ground state potential, as well as other recent experimental and theoretical progress in the field will be reviewed. The relationship of photoassociation spectroscopy to recent experiments on the Bose-Einstein condensation of alkali vapors will also be discussed.

[1] P. Lett, P. Julienne, and W. Phillips, Annu. Rev. Phys. Chem. **46**, 423-452 (1995); D. Heinzen, in *Atomic Physics 14*, .(AIP Press, 1995)., p369.

[2] K. M. Jones, S. Maleki, L. P. Ratliff, and P. D. Lett, J. Phys. B (1996).

M1

OZONE : FIRST OBSERVATIONS OF $v_2 = 3$ STATES
THROUGH INFRARED HIGH RESOLUTION SPECTRA

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Using new high quality high resolution spectra of ozone with $p = 25$ Torr, $L = 32$ m, $S/N \cong 600$, resolution 0.008 cm^{-1} we have been able to observe very weak hot bands involving $v_2 = 3$ states : $3v_2 - v_2$ (1400 cm^{-1}), $3v_2 + v_3 - v_2$, $v_1 + 3v_2 - v_2$ (2400 – 2500 cm^{-1}), and $v_1 + 3v_2 + v_3 - v_2$ (3400 cm^{-1}). The values of energy levels, with J up to 35 and K_a up to 10 are confirmed by the observations of $3v_2 + v_3$ (3100 cm^{-1}) and $v_1 + 3v_2 + v_2$ (4100 cm^{-1}).

We present here the results of Hamiltonian constants for the upper states of these bands as well as the study of v_2 behavior of A, B, C and Δ_K constants, the dependence being quasi linear.

These results are of first importance for the knowledge of potential function and the extrapolation to $v_2 = 4$ and $v_2 = 5$ states which perturb others observed states, due to the proximity $\omega_1 + \omega_3$ & $3\omega_2$.

M2

The Structure of Azulene as Determined
by Fourier Transform Microwave Spectroscopy

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The microwave spectra of ^{13}C isotopomers of azulene in natural
abundance have been measured in a pulsed nozzle Fourier transform
microwave (FTMW) spectrometer over the 8–18 GHz range. In addition,
1-d_1- and 1,3-d_2-azulene have been investigated in mixtures with variable
deuterium content. The rotational transitions of the parent species have
been remeasured at higher resolution with the FTMW spectrometer.
Because of the low vapor pressure at ambient temperature of azulene,
argon as the buffer gas at pressures around 2 bar was saturated with
azulene in a heated inlet system at a temperature of 125°C.

Rotational and centrifugal distortion constants have been fitted to
the measured frequencies of the rotational transitions of all measured
isotopomers. The corresponding moments of inertia have been used to
determine the positions of all carbon and one set of equivalent hydrogen
nuclei. The carbon coordinates define the geometry of the planar non-
alternating aromatic ring system of azulene completely. A single set of
transitions has been observed for the asymmetrically 1-, 4-, 5- and 9-^{13}C
substituted isotopomers with twice the intensity as for the symmetrically
2- and 6-^{13}C substituted isotopomers. This fact is direct evidence for
the C_{2v} covering symmetry of azulene.

High S/N FT-IR Emission Setup for the Range 300-11000 cm^{-1}.

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We report an experimental setup for gas emission measurements in the infrared using the high resolution Fourier-Transform spectrometer Bruker 120HR at Giessen. The setup consists of an oven and a heated cell with the following features:

a) Aspects designed for emission work:
  - Adjustable aperture mounted in the spectrometer vacuum for blocking out the oven wall emission
  - New detector chamber setup to minimize the number of mirrors between the emission cell and detector
  - Cooling system for the cell windows
  - Full vacuum transfer optics from emission cell to the spectrometer

b) Optimization for different infrared regions:
  - Windows: CsJ, KBr or CaF$_2$
  - Detectors: Ge:Cu, InSb or Ge
  - Filters: New 4K cooled optical filter changer for 12 filters for the Ge:Cu detector covering the range 300-1800 cm-1

c) Options:
  - Possibility of using the same setup for hot absorption experiments
  - Oven temperature variable up to 1700 C.
  - Cells: quartz or alumina
  - Static or flow measurements

Using this experimental setup we have measured high S/N spectra of several molecules. We report here measurements of HCN, H^{13}CN, HC^{15}N, H^{13}C^{15}N, DCN, D^{13}C^{15}N in the ν_2 region, 400-800 cm^{-1}, with a resolution of 0.005 cm^{-1} and S/N≈1000, measurements of HCN, H^{13}CN, HC^{15}N, H^{13}C^{15}N in the $2\nu_1$ region, 6000-6600 cm^{-1}, with a resolution of 0.05 cm^{-1} and S/N≈5000, and the assignment of the $2\nu_1$ band. Other posters[1,2] at this conference report the assignment for HCN and D^{13}C^{15}N in the ν_2 region.

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[1]Poster: G. Ch. Mellau, M. Winnewisser, S. Klee, W. Quapp, M. Hirsch, A. Maki, An Emission Measurement Of Bending Mode Hot Bands of D^{13}C^{15}N

[2]Poster: G. Ch. Mellau, M. Winnewisser, A. Maki, Emission Spectrum of HCN at 1400 K in the Region of the Bending Fundamental

AN OPTIMIZED WHITE-TYPE GAS CELL FOR THE BRUKER IFS 120 HIGH RESOLUTION FTIR SPECTROMETER

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Recently we have furnished our Bruker spectrometer with a large (300 l) long path cell (up to 200 m)[1]. Now we have completed the construction of another White cell with a much smaller volume. The construction and properties of this cell are described. When designing the optics of the cell the model proposed by W.H. Kohn[2] has been used to minimise astigmatism caused by off-axis imaging processes at spherical surfaces. The absorption path length of the cell is adjustable in the range of 3.2 - 41.6 meters and the volume is about 20 litres. Measurements show that the transmission losses of the cell are accounted for by reflection losses at the gold coated mirrors. The construction of the cell is such that it can be connected to a similar Bruker instrument which is utilising a synchrotron radiation source at MAX laboratory in Lund.

The cell has been successfully tested by measuring the v_2 band of CS_2 at 400 cm^{-1} in Oulu with our recently updated spectrometer and the $v_1 - v_2$ band of $^{13}CS_2$ at 274 cm^{-1} in Lund. In the v_2 measurement we attained the resolution of 0.0011 cm^{-1} and the signal-to-noise of about 60 with a total recording time of 49 hours and absorption path length of 3.2 m. In the second test with synchrotron radiation in Lund, practically the same resolution was attained with a path length of 9.6 m.

[1] T.Ahonen *et al.*, J. Mol. Spectrosc. 181, 279-286 (1997)

[2] W. H. Kohn, Appl. Opt. 31, 6757-6764 (1992)

A FIR Laser Magnetic Resonance Spectrometer for Measuring Radicals of Atmospheric Relevance

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Radicals play a key role in the chemistry of earths atmosphere. But there is still a lack of compact and versatile in-situ detectors for these reactive and short living species. A far-infrared (FIR) laser magnetic resonance (LMR) spectrometer is a promising tool for this purpose because of its high sensitivity and specifity. Most radicals which are abundant in the atmosphere such as OH, HO_2 and ClO can be detected qualitatively and quantitatively in mixed gaseous samples by this method.

At the DLR Institute of Space Sensor Technology a FIR-LMR spectrometer is under development. The spectrometer will be used as an in-situ sensor for radicals in the lower stratosphere and upper troposphere. Target molecules are OH and HO_2. The spectrometer will be used aboard of the Falcon a DLR owned airplane for atmospheric research.

The spectrometer is based on an optically pumped FIR laser which is optimised for the frequency range of 1.5 to 6 THz. In this region OH and HO_2 have their strongest absorptions. A superconducting magnet with a maximum flux density of 3 T produces a 12.5 cm long homogeneous field region. The magnet is located inside a cryostat with a 50 mm inner diameter room temperature bore. The design of the spectrometer, its performance and first laboratory measurements will be presented.

In addition, first results of a FIR-LMR spectrometer which utilizes permanent magnets in order to achieve the Zeeman tuning are described. Despite the fact that the flux density is limited well below 1 T and the field homogeneity is not as good as for an electromagnet or a superconducting magnet this is an attractive alternative. An LMR spectrometer based on permanent magnets is smaller, has less weight and less power consumption and is easier to handle than conventional spectrometers. Using such a system for field measurements seems to be feasible.

M6

SPECTROSCOPY OF CARBON SPECIES C_4 - C_{15}, C_4^- - C_{12}^-, C_{14}^-, C_{16}^-, C_{18}^- AND C_{20}^-

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Over the last few decades a number of research groups have utilised a variety of methods to characterise the electronic, vibrational and rotational energy levels of charged and neutral carbon molecules. Even in the early days the spectroscopic study of these species was undertaken with the help of the matrix isolation technique[1], and this method is widely regarded as a useful link between *ab initio* calculations and the gas phase approach. In recent years a wealth of new assignments were also provided by using a combination of mass selection and matrix isolation.

The astonishing outcome of such experiments has been the observation of several excited electronic states not only of neutral but also of anionic carbon chains. In addition vibrational frequencies of the upper electronic states were measured and some infrared active modes of vibration determined. Reference 2 is given as an example for results obtained.

[1] D. E. Milligan, M. E. Jacox and L. Abouaf-Marguin, J. Chem. Phys. 46 (1967) 4562; D. E. Milligan and M. E. Jacox, J. Chem. Phys. 51 (1969) 1952.

[2] D. Forney, P. Freivogel, M. Grutter and J. P. Maier, J. Chem. Phys. 104 (1996) 4954.

PRESSURE BROADENING AND SHIFT COEFFICIENTS IN THE $2\nu_2^0$ AND ν_1 BANDS OF $^{16}O^{13}C^{18}O$

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In this paper we report the first measurements of pressure broadening and pressure-induced line shifts by air and by N_2 in the $2\nu_2^0$ and ν_1 bands of $^{16}O^{13}C^{18}O$. Broadening and shift coefficients at room temperature were determined for 93 rovibrational transitions in each band. The results were obtained by analyzing ten long-path high-resolution absorption spectra using a multispectrum nonlinear least-squares fitting technique.[1] The broadening coefficients were approximately the same for transitions having similar rotational quantum numbers in each band, but the N_2-broadening coefficients were about 4 percent larger than the air-broadening values. In contrast to the broadening coefficients, the pressure-induced line shift coefficients were found to be transition-dependent; different shifts were obtained for P- and R-branch lines having the same J" value. Except for a few R-branch lines, the measured shift coefficients were negative; values ranged from approximately -0.006 to +0.004 cm^{-1} atm^{-1} at 296K. No significant differences were observed between the shift coefficients of the two bands or the two broadening gases. Our results have been compared with those reported in the literature for the more abundant $^{12}C^{16}O_2$ species.

[1]D. Chris Benner, C. P. Rinsland, V. Malathy Devi, M. A. H. Smith, and D. Atkins, JQSRT 53, 705-721 (1995).

M8

Time resolved Measurement of Nitric Oxide in human
breath by Faraday LMR Spectroscopy

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The significance of Nitric Oxide in many different kinds of medical and pharmacological processes has only been known for a few years and has increasingly gained more interest.

Especially in the upper and lower respiratory tract NO plays an important role in several physiological and pathophysiological mechanisms of regulation. To understand these processes it's necessary to know which quantity of NO is released at the various parts of the respiratory tract. This requires a method of measurement that provides for a good time resolution and a high sensitivity. These and further advantages, for example the possibility to distinguish between different isotopomers, are given by the Faraday Laser Magnetic Resonance Spectroscopy.

In a series of measurements with eight healthy subjects the NO-concentration in the exhaled breath was measured as well as the flow rate. The quantity of NO was determined varying the following parameters: time of inhaling and exhaling, time of holding breath before exhalition, inhalition of NO-free or NO-containing air, breathing through mouth or nose. The results show characteristic features which are strongly related to these parameters. Precise information about the quantitative NO release can be derived from these findings. For example, the highest concentration of NO (up to several hundred ppb) is found in the nasal mucous membrane.

M9

Line-broadening parameters in the
ν_4 and ν_3 bands of $^{12}CH_4$

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We have performed semi-classical line-broadening coefficients calculations in the ν_4 and ν_3 bands of $^{12}CH_4$ with mainly a rare as the perturber.

In coherence with the tetrahedral formalism[1], we have implemented a symmetrized version of the semi-classical theory initially developed by ROBERT and BONAMY[2]. Details on the construction of the potential model and on the derivation of the interruption function for the XY_4- atom case as well as typical results have already been reported[3].

Comparisons of the calculations with the available experimental line-broadening coefficients will be presented. Related works on individual state to state rotational relaxation rate constants calculations and experimental investigations on the $SiH_4 - Ar$ system will also be presented.

[1] J.-P. CHAMPION, M. LOËTE. and G. PIERRE. *Spherical Top Spectra.* In K. NARA-HARI RAO and A. WEBER, editors, *Spectroscopy of the earth's atmosphere and interstellar medium*, pages 339–422. Academic Press Inc. U.S.A., 1992.

[2] D. ROBERT and J. BONAMY. J. Phys., **40**(10), 923–943, (1979).

[3] T. GABARD. Thèse, Université de Bourgogne, Dijon, France, 1996; T. GABARD. J. Quant. Spectrosc. Radiat. Transfer, **57**(2), 177–196 (1997); T. GABARD. To appear in J. Quant. Spectrosc. Radiat. Transfer.

M10

EXTRACTION OF VIBRATIONAL DISTRIBUTION FUNCTIONS AND ROTATIONAL TEMPERATURES FROM HIGH RESOLUTION EMISSION SPECTRA EMITTED BY A NON UNIFORM MEDIUM

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The by-now-standard method of inferring vibrational populations from partially or fully rotationally resolved optical spectra is based on the construction of a synthetic spectrum at a given temperature which is least squares fitted to the experimental one. The rotational temperature is determined iteratively and corresponds to the minimum of the aggregate squared error between experimental and synthetic spectra. This method is of physical significance only if the measured optical emission is mainly emanating from a homogeneous volume whose parameters are nearly constants. This hardly occurs in real experiments, where molecule density and temperature gradients are usually of considerable magnitude. In the present work a method is developed to recover from a high resolution optical spectrum the vibrational distribution functions from zones at different temperatures. The proposed procedure is of special importance in studying elementary processes involving vibrationally excited particles, if the rate constants of these processes have a strong dependence on the translational temperature .The method is applied to retrieve the vibrational distributions functions and rotational temperatures in optically excited V-V pumped CO.

STUDY OF VIBRATIONAL RELAXATION OF ν_3 STATE OF O_3
DUE TO COLLISIONS WITH NOBLE ATOMS

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The results of measurements of vibrational relaxation rate constants of selectively excited ν_3 state of O_3 molecule in binary mixtures with He, Ne, Ar, Kr, and Xe are reported. The measurements were made by using the high sensitive photoacoustic detector with frequency tunable CO_2 laser. The phaseshift between oscillations of acoustic pressure within photoacoustic cell and the oscillations of the excited radiation intensity was measured as a function of the total pressure of gas mixture.

The procedure of fitting of experimental and calculated values of the phaseshift was used to determine the main rate constants of the process of ν_3 state relaxation like K_{D2} describing the energy exchange between ν_3 and ν_2 states, and K_2 and K_D describing the collisional relaxation of ν_2 and ν_3 to the ground vibrational state.

The obtained values of K_{D2}, for example, vary from 3200 $s^{-1}.Torr^{-1}$ for O_3-He collisions to 200 $s^{-1}.Torr^{-1}$ for O_3-Xe ones. The obtained results are compared with theoretical estimations and discussed.

M12

COLLISIONAL PROCESSES OF C_2H_2 PERTURBED BY Xe: SPEED DEPENDENT BROADENING EFFECT ON THE LINESHAPE

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Several P- and R-branch infrared absorption lines of the ν_5 band of C_2H_2, diluted in Xe at pressures ranging from 40 to 300 mbar, have been recorded at high resolution using a tunable diode-laser spectrometer. Their lineshapes have been analyzed by mean of models including either a narrowing by Dicke effect or by a speed dependence of the collisional broadening[1]. None of these models have given satisfactory results over the full pressure range of the perturber. It is shown that a correct treatment must include both line narrowing effects. This has been done, at first, by considering a general hard-collision profile, for which speed dependence of the collisional broadening is modelized by an inverse power law interaction potential[2]. In a further step we propose an extension of the ideas developped by Berger *et al.*[3]. The speed dependence of the collisional contribution is rigorously deduced for each line under study, by mean of the relative speed dependence of the collisional cross section, obtained from semi-classical calculations. This speed dependence is then re-injected in the lineshape model so that consistent results are obtained.

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M13

GLOBAL FITTING OF CO_2 VIBRATIONAL-ROTATIONAL LINES
USING THE EFFECTIVE HAMILTONIAN APPROACH

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About 13000 experimental lines of the principal isotopic species of CO_2 selected from literature sources have been fitted to about 100 parameters of a reduced effective Hamiltonian built up to sixth order in the Amat-Nielsen ordering scheme. This Hamiltonian has been obtained from an effective Hamiltonian describing globally all vibrational-rotational energy levels in the ground electronic state and containing in explicit form all resonance interaction terms due to the approximate relations between harmonic frequencies $\omega_1 \approx 2\omega_2$ and $\omega_3 \approx \omega_1 + \omega_2$. RMS deviation of 0.001 cm^{-1} has been achieved in the fitting. In order to test its predictive capabilities, the model has been used to calculate the line positions of six bands: $05511 \rightarrow 05501$, $1331(1,2) \rightarrow 1330(1,2)$, and $2111(1,2,3) \rightarrow 2110(1,2,3)$, which are compared with experimental lines measured in emission spectra using a Fourier Transform Spectrometer. The importance of the resonance Coriolis interaction for the calculation of the line positions of some bands has been demonstrated and the prediction of the line positions of the corresponding bands in the HITRAN database have been improved upon.

M14

"SUPERCOMBINATION DIFFERENCIES" AND ITS APPLICATIONS FOR THE PROBLEMS OF HIGH RESOLUTION VIBRATION-ROTATIONAL SPECTROSCOPY OF SYMMETRIC TOP MOLECULES: CHD_3 MOLECULE

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Method, called as the "supercombination differencies", has been derived in order to determine the $A_1 - A_2$ ($K = 3$) ground state splittings in symmetric top molecules from their infrared spectra, and was applied to the study of CHD_3 molecules.

High reolution Fourier transform spectra of 12 rotation-vibrational bands (ν_3, ν_6, ν_5, $2\nu_5$(al), $2\nu_5$(e), $2\nu_3$, $2\nu_6$(al), $2\nu_6$(e), $\nu_3 + \nu_6$, $\nu_3 + \nu_5$, $\nu_3 + \nu_6$(al), and $\nu_3 + \nu_6$(e)) were used for the construction of "supercombination differencies" and determination of "experimental" values of $A_1 - A_2$ ($K = 3$) splittings in the ground vibrational state. Parameters $2h_3 = 2.2960 \pm 0.0090* 10^{-10}$ cm^{-1} was found which reproduced experimental values of splittings for $J \leq 20$ with the accuracies closed to experimental uncertainties.

Possibility of simultaneous determination of "epsilon" and h_3 parameters (ambiguous parameters of Watson's ambiguity theory, J.K.G. Watson, in "Vibrational Spectra and Structure", Ed. : J. Durig, Elsevier, Amsterdam, 1977) of the CHD_3 molecule is discussed. It is shown that this problem can be positively solved on the base of analysis of high resolution rotational structure of the ν_5 band. In this case, the ν_5 band is theoretically analysed and its rotational structure is reproduced with the accuracies equal to experimental uncertainties for $J^{(upper)} \leq 25$ and $K^{(upper)} \leq 25$.

New set of ground state rotational energies of the CHD_3 molecule is determined, which allowed us to explain some effects and pecularities in infrared spectra, which earlier were not explained (in particular, $A_1 - A_2$ splittings with $K^{(upper)} = 1, 2, 4, 5, 7$ in the ν_5 and $\nu_3\nu_6$ bands).

M15

RELATIONS OF LOCAL AND NORMAL MODE MODELS IN

PYRAMIDAL XH$_3$ TYPE MOLECULES

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The relations of the spectral parameters of local and normal mode
models of XH$_3$ type molecules have been derived for both the
stretching and the bending degrees of freedom including Fermi
resonance interactions. Since in the local mode model there are fewer
parameters than in the normal mode model, the so called x-K relations
are obtained in the normal mode model. In the case of bending, these
relations are not well obeyed. This may mean that physically the best
model could be a combination of the local and normal mode models in
the sense that one would use unsymmetrized internal coordinates for
the stretches and symmetrized internal coordinates for the bends.
Spectral parameters for this semilocal mode model are presented and
the corresponding relations of these and normal mode parameters are
derived.

M16

SYMMETRY ADAPTED ALGEBRAIC APPROACH TO MOLECULAR VIBRATIONAL SPECTROSCOPY

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A symmetry adapted algebraic model of molecular vibrations is presented which is specially suited for the description of molecules displaying high symmetry. Its main features are that:

I)   it incorporates anharmonic effects locally through the use of $SU(2)$ algebras,

ii)   it provides a systematic procedure to construct all physically meaningful interactions in terms of $SU(2)$ generators,

iii)   there is a direct connection to configuration space interactions, and

iv)   spurious states can be removed exactly.

We illustrate the model with applications to CH_4.

Quantum and Semiclassical calculations of line broadening coefficients for $S_0(J)$ lines of H_2-He and H_2-Ar at high temperature. Comparisons with experiment.

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Quantum close-coupling (CC) and semiclassical (SC) calculations of broadening and shifting coefficients of $S_0(J)$ lines of H_2-He have been performed up to 3000K using an *ab initio* potential energy surface [1]. The agreement between the theoretical results and experimental data available up to 1000K (SRS measurements performed in Dijon) is very good for the broadening coefficient γ and reasonable for the shift δ. The main interest is to test the validity of the semiclassical method versus CC calculation on a wide range of temperature. The agreement is very satisfactory. Further the SC model permits a detailed analysis of the mechanisms involved in the temperature dependence of the molecular parameters γ and δ. Similar investigations for H_2-Ar, using the PES of Le Roy et al [2] will be also presented in the poster.

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A theoretical investigation of hydrogen-bonded complexes of type $NH_3 \cdots H-C\equiv X$ (X = N, CH, C_3H and $C-CH_3$)

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A systematic investigation of hydrogen-bonded complexes with ammonia as proton acceptor has been carried out by means of the coupled electron pair approximation (CEPA). The equilibrium dissociation energies D_e are predicted to be 12.4 kJ mol^{-1} ($H_3N\cdots HCCCH_3$), 15.0 kJ mol^{-1} ($H_3N\cdots HCCH$), 17.7 kJ mol^{-1} ($H_3N\cdots HC_4H$) and 25.8 kJ mol^{-1} ($H_3N\cdots HCN$). The corresponding equilibrium intermolecular separations R_e (N $\cdots$ H) are 2.359, 2.301, 2.264 and 2.134 Å, respectively. Within the harmonic approximation, the bathochromic shifts of the CH donor stretching vibration are 93.4, 77.2 (75.1), 125.4 (127.4) and 197.1 (200.9) cm^{-1}, where experimental values [1] [2] are given in parentheses. The corresponding absolute IR intensities (in km mol^{-1}) are 261, 300, 423 and 495. The NH_3 umbrella vibration experiences hypsochromic shifts of 23, 29, 34 and 59 cm^{-1}. Complex formation lowers the intensity of the NH_3 symmetric stretching vibration which will thus be difficult to observe. Within a five-dimensional model which explicitely takes the totally symmetric modes into account, anharmonicity effects were studied for $NH_3\cdots HCN$.

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Spectrometry of the Oxygen Molecule Dimer

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Spectra of the oxygen molecule dimer, a Van der Waals dimer involving
open shells, were obtained by intra-cavity laser absorption spectroscopy (ICLAS)
using either an intracavity slit jet (length 25 cm, width 10 cm) or a cell cooled at
liquid nitrogen temperature. Two broad absorption bands were recorded, (0-0)
centered at 629 nm, and (1-0) centered at 578 nm, corresponding respectively to
the transitions:

$$
\left[O_2\left({}^1\Delta_g\right)_{v=0} - O_2\left({}^1\Delta_g\right)_{v=0} \right] \leftarrow \left[O_2\left({}^3\Sigma_g^-\right)_{v=0} - O_2\left({}^3\Sigma_g^-\right)_{v=0} \right]
$$

$$
\left[O_2\left({}^1\Delta_g\right)_{v=0} - O_2\left({}^1\Delta_g\right)_{v=1} \right] \leftarrow \left[O_2\left({}^3\Sigma_g^-\right)_{v=0} - O_2\left({}^3\Sigma_g^-\right)_{v=0} \right]
$$

Rotational structure was observed for the first time. Even working at 10-20 K in a
supersonic jet or at 77 K in a cold cell, the spectra (recorded at a resolution ≈ 0.05
cm^{-1}), show many line superpositions, complicating the analysis of the rotational
structure.

The main features in the spectrum have been analysed. We have calculated
the rotational structure of the dimer in its lowest and excited states using a
complete quantum calculation (LC-RAMP), including all terms of coupling and
anharmonicity. A system of radial coupled equations of the Hamiltonian
describing the motion of the nuclei has been solved in a basis of linear
combinations of radial and angular functions. The J dependence is very similar to
that of a rigid rotor. An estimation of the rotational constant and hence of the
equilibrium separation *Re* in the dimer will be given. A simulation of the (0-0)
band at different temperatures will be compared to experimental spectra.

THE $B^1\Pi \sim C^1\Sigma^+$ PERTURBATION IN KLi

STUDIED BY HIGH RESOLUTION LASER SPECTROSCOPY

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The $B^1\Pi–X^1\Sigma^+$ band system of the KLi molecule was studied by Doppler-free polarization spectroscopy technique in a heat-pipe oven[1,2]. The *e*-parity rovibronic levels in the B state were found to be subject to rotational perturbations, assigned to interaction with the $C^1\Sigma^+$ state. The observed vibrational variation of perturbation matrix elements was used to determine the absolute vibrational numbering in the C state. The deperturbation analysis provided molecular constants of the $B^1\Pi$ and $C^1\Sigma^+$ states.

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FTS EMISSION SPECTROSCOPY
APPLICATION TO SIF

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The emission spectrum of the SiF radical has been recorded from 9.000 to 23.000 cm^{-1} using a Fourrier Transform Spectrometer.

As emission spectra show a lack of energy compared to absorption spectra it is shown that the recording of the total signal is to be preferred to the use of AC part of the signal. In order to yield better defined constants we also use line intensities to weight line positions in the different band fittings. The advantages of weighted fittings are shown in the study of four electronic systems : $A^2\Sigma^+ - X^2\Pi_i$, $D'''^2\Sigma^+ - C'^2\Pi$, $C'^2\Pi - B^2\Sigma^+$ and $D'^2\Pi - B^2\Sigma^+$

M22

BrCNO as a Semirigid Bender

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Very recently, Lichau *et al.*[1] have measured and analyzed the rotational spectrum of the BrCNO molecule. They were able to identify transitions within the vibrational ground state together with more than 30 vibrational satellites for both the ^{79}BrCNO and ^{81}BrCNO isotopomers. Most of the vibrational satellites are assigned to excited states of the low-lying Br–C–N bending mode. The irregular variation of the rotational energy spacings with excitation of the Br–C–N bending mode indicates this mode to be very floppy; BrCNO is *quasilinear*. We are in the process of carrying out an *ab initio* calculation of rovibrational energy levels associated with the Br–C–N bend. The bending potential curve is being calculated by means of the MRD-CI *ab initio* method, and we will use this potential to carry out a *semirigid bender* calculation of the bending-rotation energies. The aim of the calculation is to confirm the vibrational assignments of Lichau *et al.*, and to provide predictions for the bending vibrational energies. We hope to present results of this work at the meeting.

[1]H. Lichau, C. W. Gillies, J. Z. Gillies, B. P. Winnewisser, and M. Winnewisser, *poster at this conference.*

ROTATIOAL SPECTRUM OF CH3OH IN THE EXCITED C–O STRETCHING VIBRATIONAL STATE

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Microwave spectrum of methanol in the C-O stretching vibrational state (v_{co}=1) has been already reported for some a-type transitions[1,2] and $k = 2 \leftarrow 1$, Q-branch lines of the E-species[1]. We observed microwave transitions in the v_{co}=1 state more systematically using a wide-scan microwave spectrometer operating in the $8-200$ GHz frequency region[3]. The observed lines are of $|k| \leq 3$, $J \leq 10$ for both the A and E-species.

Microwave spectral lines in this vibrational state were also studied by infrared–microwave double resonance method in the $30-100$ GHz frequency region. As an infrared source, a microwave modulator of a CO_2 laser was used. Rotational transitions in the v_t=0, 1 and 2 states were observed.

All the observed frequencies were analyzed to refine the Taylor expansion coefficients for vibration-rotational terms[4] and to determine molecular constants of methanol in the v_{co}=1 state.

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M24

MOLECULAR BEAM FOURIER TRANSFORM MICROWAVE SPECTROSCOPY.

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We present a newly built Fourier transform microwave spectrometer running in the 4-18 GHz frequency region, coupled to a pulsed supersonic jet. It consists of a Fabry-Perot resonator with spherical mirrors, 40 cm diameter and 80 cm radius curvature. The microwave signal is amplified and downconverted from the microwave to the radio frequency region. This operation is done in two steps. An intermediate frequency of 30 MHz for the first mixing is used and a second one of 2 MHz. This signal is fed into a 100 MHz numeric oscilloscope. Data are transferred into the central memory of a PC computer, which operate the fast Fourier transform in order to give the rotational spectrum. First spectroscopic studies will be presented :

Chloroform ($CHCl_3$)
Hyperfine componants of the $J = 0 \rightarrow 1$ and $J = 1 \rightarrow 2$ lines of $CH^{35}Cl_3$ and $CH^{37}Cl^{35}Cl^{35}Cl$ isotope where observed with an excellent resolution (HWHM = 3kHz).

Vinylarsine (CH_2CHAsH_2)
Low J transitions of the vinylarsine (CH_2CHAsH_2) syn form has been observed which enable us to determine spin-rotation constants and elements of the quadrupole tensor.

Atmospheric polluants
For atmospheric polluant detection purpose, comparison sensitivity tests have be done for butane, propane and tetrahydrothiophene gases. The sensitivity decreases by a factor between 20 and 30 when using air rather argon like carrier gas. These values are in agreement with previous measurements[1].

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THE ROTATIONAL SPECTRUM OF BrCNO,
AN EXTREMELY QUASILINEAR MOLECULE

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The rotational spectrum of the unstable molecule bromo fulminate, BrCNO, was recorded in the spectral ranges $52\,\text{GHz} - 79\,\text{GHz}$, $117\,\text{GHz} - 148\,\text{GHz}$, and $160\,\text{GHz} - 179\,\text{GHz}$ using a BWO based millimeter wave spectrometer with a free space absorption cell. The sample was generated at the inlet of the cell by gas phase pyrolysis of dibromoformaldoxime, Br_2CNOH [1]. Using relative intensities and the l-dependence of the bromine quadrupole splitting, we have been able to identify the ground state and more than 30 vibrational satellites for the $^{79}BrCNO$ isotopomer as well as for the $^{81}BrCNO$ isotopomer. Most of the satellites have been assigned to excited states of the low lying Br–C–N bending mode. The pattern formed by these satellites clearly indicates that BrCNO is a very quasilinear molecule, most likely slightly more bent than C_3O_2. From analysis of the l-type doubling constant q_5, the first excited bending state is estimated to be less than $25\,\text{cm}^{-1}$ above the ground state. The relative intensities of the rotational transitions confirm this result.

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M26

EFFECTS OF ELECTRON-SPIN ON ROTATIONAL SPECTRA OF WEAKLY-BONDED OXYGEN COMPLEXES

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Few years ago, we developed a model[1] for calculating the ro-vibronic energy levels of a near rigid nonlinear open-shell complex consisting of an open-shell diatomic molecule molecule (of $\Lambda = \Sigma$, Π, Φ etc. and of $S \geq \frac{1}{2}$) van der Waals bonded to a closed-shell partner. We have applied this model to analysis and fitting the infrared spectrum of the O_2HF/O_2DF complex[2] and the microwave spectrum of the $O2-SO_2$ complex[3]. Results of these preliminary fits show that effects of electron-spin on the rotational structure are significant in O_2-HF, such that the spectrum consists of triplets which correspond to the $\Sigma = 0$, ± 1 spin-components of the ground electronic state $\left(^3\Sigma_g^-\right)$ of O_2. Preliminary analysis of the microwave spectrum of the O_2-SO_2 complex shows that all
transitions originate from the lowest energy spin state ($\Sigma = 0$) and that tunnelling, of monomers within the complex, causes large shifts in positions of the rotational lines. In addition, for both complexes, the electron-spin and the rotational parameters are strongly correlated. We have introduced some modifications to our original model[1] to reduce the correlation problem and to take tunneling, in a phenomenological way, into account. Such modifications led to improvement in standard deviations of the fits but we still have a problem in fitting several weak lines in the infrared spectrum of O_2-HF and in interpreting the physical meaning of the molecular parameters that are required for fitting the O_2-HF and the O_2-SO_2 data. At this meeting, we present the modified forms of the model, results of our preliminary fits for the O_2-HF and the $O_{,-}$ O_2-SO_2 complexes[2,3], and suggestions for solving the problems concerning these fits.

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EXCITED VIBRATIONAL STATES OF BENZENE: HIGH RESOLUTION FTIR SPECTRA AND ANALYSIS OF SOME OUT-OF-PLANE VIBRATIONAL FUNDAMENTALS OF C_6H_5D

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There exist only few studies yet of rotationally resolved infrared spectra of asymmetric top benzene isotopomers. We have studied , for instance, $^{12}C_5{}^{13}CH_6$ in natural abundance in our investigation of C_6H_6 [1]. In the case of C_6H_5D there exists no rotational analysis of any vibrational band, so far. We have measured the infrared spectra of the ν_4, ν_{10b} and ν_{11} fundamental bands of C_6H_5D in the range 540-830 cm^{-1} with an instrumental band width of 0.0024 cm^{-1} (unapodized FWHM) using a Bomem DA 002 Interferometric Fourier Transform spectrometer. The rotational analysis for ν_4 yields ground state constants by combining ground state combination differences and published microwave data [2]. Excited state constants for the ν_4 level were obtained up to quartic terms, using Watson's A-reduction Hamiltonian in the III^r representation [3,4], resulting in a band center $\tilde{\nu}_4^0 = 697.593$ cm^{-1}. A partial analysis is presented for the ν_{10b} fundamental ($\tilde{\nu}_{10b}^0 = 778.027$ cm^{-1}), which appears to be locally perturbed by the $\nu_{16a} + \nu_{16b}$ combination band. The very strong ν_{11} band is strongly perturbed, most probably by ν_{6a} and ν_{6b}. The results are discussed in relation to comparison with accurate ab initio electronic structure calculations including non Born-Oppenheimer effects as well as potential applications with isotope tracer detection and infrared laser chemistry.

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ROTATIONAL SPECTRUM OF AMINO-CYCLOBUTANE

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The rotational spectrum of amino-cyclobutane has been investigated by using a free jet and a room temperature spectrometers. An equatorial conformer with the amino lone pair *gauche* with respect to the adjacent hydrogen of the ring has been assigned. Large splittings related to the amino group large amplitude motions have been measured.

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The $\nu_6 + n\nu_9$ Levels of Dicyanoacetylene (NCCCCN)

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In a previous paper[1] we have given experimental data for some components of the bands $\nu_6 + (n+1)\nu_9 - n\nu_9$ (with $n = 0$ to 7, $\Delta\ell = 0$). Now we have identified a series of bands $\nu_6 + n\nu_9 - (n+1)\nu_9$ (with $n = 0$ to 5, $\Delta\ell = 0$, and $\ell = n+1$). These bands correspond to different ℓ-components in the upper state levels, and it has become possible to calculate the ℓ-type resonances in the level series $v_6 = 1, v_9 = 1, 2$, and 3.

As already stated in Ref.[1] only one of the possible transitions to $v_6 = 1, v_9 = 2(\ell = 1)$ respectively $v_6 = 1, v_9 = 3(\ell = 0$ and 2) seem to be observable. Effective ro-vibrational constants for the levels obtained from models including rotational resonance shall be presented. They are in reasonable agreement, but some additional influence from vibrational levels nearby is not accounted for in our model.

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M30

HCCH OVERTONE STATES BY LASER INDUCED
DISPERSED FLUORESCENCE IN THE INFRARED
RANGE

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We have applied the method of laser induced fluorescence (LIF) to study
highly excited vibrational overtones in molecules in the near infrared
range. This method offers some advantages compared to conventional
one-photon absorption techniques. For example, it gives us an access to
vibrational states which cannot be populated by one photon transitions
from the ground state. Up to now the LIF method has been successfully
utilised for electronic transitions in atoms and molecules. We have
developed a dispersed laser induced fluorescence method for the detection
of weak rovibrational transitions in the electronic ground state and applied
it to the HCCH molecule. The cell containing the sample has been placed
inside a Ti:sapphire ring laser cavity and fluorescence signal has been
collected by a parabolic mirror and directed into a high resolution FTIR-
spectrometer. By pumping single vibration-rotation lines we have
measured the dispersed fluorescence from $v_1 + 3v_3$ (Σ^+_u) to $v_1 + 2v_3$ (Σ^+_g) in
acetylene in the $2800 - 3300$ cm^{-1} range. Besides two expected
rovibrational transitions from the upper state many collision-induced
transitions have been observed per one pumping line. The work on
analysing the dispersed fluorescence and collision-induced transitions is in
progress and the latest results will be presented at the conference.

M31

ANHARMONIC CONSTANTS AND FUNDAMENTAL FREQUENCIES OF $^{12}C_6H_6$

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The gas phase infrared spectrum of $^{12}C_6H_6$ has been recorded between 400 and 6000 cm^{-1} at the resolution of 0.008 cm^{-1}, on a *BOMEM DA2* interferometer to analyse the satellite bands accompanying the fundamentals and combination bands of the molecule. The wavenumbers of the Q-branches of these hot bands depend on the anharmonic constants x_{ij}, g_{ij} and on the vibrational l doubling constants R_{ij} and S_{ij} (fig.1). The analysis is done on the parallel bands by comparison with the theoretical anharmonic constants calculated in Ref.[1] . Here we present the complete list of experimental anharmonic constants determined up to now, that come or from the analysis of infrared spectra, either from raman and electronic spectra already published. The wavenumbers of the v_6, v_7, v_8 and v_{19} fundamentals (Herzberg numbering) obtained with improved accuracy from sum and difference bands of the IR spectrum are reported. The effect of Fermi interaction on the wavenumber of satellite bands is taken into account .
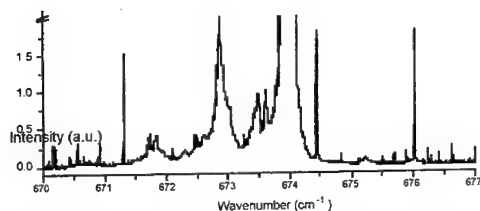
Fig. 1 : Q branches of the only fundamental parallel band of benzene ; the position of the satellites is given by the anharmonic constants.

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$D^2\Sigma^+(v=0,1) \to A^2\Pi(v=0\text{-}3)\sim B^2\Sigma^+(v=0\text{-}3)$ TRANSITIONS
OF
STRONTIUM MONOIODIDE

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Fourier transform spectra of the laser-induced fluorescence of strontium monoiodide have been recorded in the visible range and analysed. SrI molecules which are obtained by dissociating SrI_3 at high temperature (about 1600 K) in a special furnace are then excited by ultraviolet lines of an Ar^{++} ion laser.

Several rotational levels of $D^2\Sigma^+$ (T_e=28944.0 cm^{-1}) are populated in the lowest two vibrational levels, either directly or after collisional relaxation, inducing fluorescence transitions ending in $A^2\Pi(v=0\text{-}3)$ and $B^2\Sigma^+(v=0\text{-}3)$. These two states are known to be in strong interaction[1], due to their small separation relative to the $A^2\Pi$ spin-orbit splitting.

The whole set of experimental wavenumbers is numerically processed in a unique adjustment and reduced to molecular constants. The interaction $A^2\Pi\sim B^2\Sigma^+$ is represented by two 15×15 (e and f) Hamiltonian matrices whose diagonal elements are described using equilibrium parameters of the states. The first five $\Delta v=0$ blocks ($v=0\text{-}4$), connected by spin-orbit and Coriolis $\Delta v=\pm 1$ interactions, are considered for a realistic representation of the $A^2\Pi(v=0\text{-}3)\sim B^2\Sigma^+(v=0\text{-}3)$ complex.

Rotational constants in $v=0$ and $v=1$ levels of $D^2\Sigma^+$ state are established for the first time. Deperturbed equilibrium molecular constants and vibration-independent interaction parameters for $A^2\Pi$ and $B^2\Sigma^+$ states are directly obtained.

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M33

INFRARED SPECTRUM OF H_3SiI IN THE 330-680 AND 1070-1360 CM^{-1} REGIONS. ACCURATE DETERMINATION OF THE GROUND STATE CONSTANTS

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High resolution FTIR spectra of H_3SiI have been recorded in the 330 $\sim$ 680 cm^{-1} (ν_3/ν_6) and 1070 $\sim$ 1360 cm^{-1} ($2\nu_6$) regions. A detailed rovibrational study was carried out for the ν_3 and ν_6 fundamental bands, $2\nu_6^{\mp2}$ and $2\nu_6^0$ overtone bands, and two hot bands $2\nu_6^{\pm2} - \nu_6^{\pm1}$ and $2\nu_6^0 - \nu_6$. A local resonance between the ν_6=2 and ν_2=ν_3=1 states was also observed.

Ground state combination differences deduced from the ν_3, ν_6, $2\nu_6^{\mp2}$ and $2\nu_6^0$ bands allowed us to obtain accurate B_0, D_J^0 and D_{JK}^0 constants. The ν_6, $2\nu_6^{\pm2} - \nu_6^{\pm1}$ and $2\nu_6^{\mp2}$ bands were used for the experimental determination of the A_0 and D_K^0 constants, whereas the hot band $2\nu_6^0 - \nu_6$ served to make internal calibration coherent. Ground state differences $\Delta_K(J) = E_0(J,K) - E_0(J,K-3)$ were calculated with K up to 12. By a least squares fit, we obtained the following results:

$A_0 = 2.842\ 603\ 7(14)$ cm^{-1} and $D_K^0 = 2.758\ 40(99) \times 10^{-5}$ cm^{-1}.

HIGH RESOLUTION RAMAN SPECTRA OF DIBORANE (B_2H_6)

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We are recording several Raman fundamental bands of diborane (B_2H_6) using the high resolution Inverse Raman spectrometer at Madrid (instrumental lineshape function FWHM ≈ 0.0025 cm^{-1}). So far the bands recorded are ν_1 (terminal B-H stretch at 2530.2 cm^{-1} for $^{10}B^{10}B$, and 2536.8 for $^{10}B^{11}B$) and ν_2 (internal B-H stretch at 2112 cm^{-1}, both $^{10}B^{10}B$ and $^{10}B^{11}B$), and we are in the process of recording ν_3 (B-B stretch at 790.0 cm^{-1} for $^{10}B^{10}B$, and 818.0 for $^{10}B^{11}B$). An analysis is in progress and will be reported at the meeting.

HIGH-RESOLUTION FTIR STUDY OF THE $v_4 + 2v_6$
ROVIBRATIONAL BAND OF **CH$_3$^{79}Br**
BETWEEN 4870 AND 5030 cm^{-1}

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* Died on March 26th 1997. He deserves here a particular homage from me
as his regular co-worker. I keep in mind that the deceased introduced me to
research activities and also taught me how to cultivate them "ex-nihilo"
in my home country.

The $v_4^{\pm1} + 2v_6^0$ and $v_4^{\pm1} + 2v_6^{\pm2}$ (E) components and the $v_4^{\pm1} + 2v_6^{\pm2}$ (A$_1$+A$_2$)
component of the CH$_3$^{79}Br isotopomer have been found and studied in high
resolution (0,006 cm^{-1})$^{(1)}$. Both (E) components are linked together and also
to the $v_2 + v_3 + 2v_4^{\pm1}$ band by anharmonic resonances, the coupling terms
being W$_1$ = 2,38 cm^{-1}, W$_2$ = 1,46 cm^{-1} and W$_3$ = 0.16 cm^{-1} respectively.
The model which has been used takes into account these three anharmonic
resonances, several ℓ (2,2) resonances perturbing the (E) components and the
x-y Coriolis interaction between $v_2 + v_3 + v_4$ and $v_3 + v_4 + v_5$ inside a 12x12
matrix. In the (A1+A2) component, only the ℓ-vibrational resonance between
~ts both upper levels has been considered. A. r.m.s deviation of 0.0065 cm-1
has been obtained through a least squares fit over 1327 lines belonging to the
three companents of $v_4 + 2v_6$ and also to the KΔK = -1 sub-band of
$v_2 + v_3 + v_4 - v_3$. Fortunately, the $v_2 + v_3 + v_4 - v_3$ and $v_3 + v_4 + v_4 - v_3$
hot bands, which have been observed around 4400 cm^{-1} $^{(2,3)}$, could give the
same informalions about involved upper levels even if the corresponding
cold bands are completely dark.

(1)   Thanks a lot for Pr. H. Bürger from the Bergische Universität of
      Wuppertal (Germany) and for Dr. G. Guelachvili from the Laboratoire
      de Physique Moléculaire et Applications, Orsay (France). They
      respectively provided the isotopically pure sample and recorded the
      spectrum which was used.
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      Spectrochimica Acta, Part A 51, 483-493 (1996)
(3)   N. Ben Sari-Zizi and C. Alamichel
      Spectrochimica Acta, Part A (in the press)

CONTACT TRANSFORMATIONS AND DETERMINABLE PARAMETERS IN SPECTROSCOPIC FITTING HAMILTONIANS

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In a number of recent least-squares fits of torsion-rotation spectra of acetaldehyde[1] and methanol[2] it was found possible to adjust more fourth-order parameters than would be expected from present contact-transformation considerations[3]. To begin our investigation of the source of this apparent contradiction between theory and practice, we have carried out numerical fitting experiments on asymmetric rotor energy levels with $J \leq 10$, which have been generated artificially from a Hamiltonian containing only quadratic and quartic operators in the angular momentum components. Even through the power series of terms in this Hamiltonian converges quickly (because of the complete absence of powers higher than four), we obtain (as expected from the caveats in Watson's original analysis[4]) a well behaved fit using an adjustable parameter set containing three quadratic rotational constants and fifteen quartic constants, *provided that* contributions from the quartic terms to the numerically generated energy levels are almost as large as contributions from the quadratic terms at $J = 10$. We have also carried out a detailed contact-transformation investigation of the algebraic "reasons" for this numerical behavior in the asymmetric rotor problem. We hope to transfer these ideas by the time of the meeting to the methyl-top internal rotor problem, where perturbation orders and convergence criteria must be applied to operators in both the asymmetric rotor problem and the internal rotor problem in a consistent way. We expect in this way to be able to explain the contradiction between theory and practice in the number of determinable torsion-rotation parameters noted above.

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HIGH-J PURE INVERSION SPECTRUM OF ND_3 IN THE $v_2=1$ STATE

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The data on the inversion spectrum in the v_2 state of ND_3[1] have been extended by measuring frequencies of high-J transitions. Highly sensitive intracavity orotron spectrometer[2] has been used for detection of week transitions between low populated states. The spectrum was investigated in the millimeter-wave region between 90 and 130 GHz at room temperature. Frequencies of pure inversion transitions ($\Delta J=0$, $\Delta K=0$) with J between 13 and 25 mainly for branches $K=J$-4, J-3, J-2 and J-1 have been measured for the first time. The new accurate experimental line positions (estimated error 30 kHz) were fitted together with previous data[1] either by the conventional polynomial expression or by an exponential expression.

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STRUCTURAL AND CONFORMATIONAL PROPERTIES OF 1,2-
ETHANEDITHIOL AS STUDIED BY MICROWAVE SPECTROSCOPY
AND *AB INITIO* CALCULATIONS[1]

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The microwave spectrum of 1,2-ethanedithiol has been re-
investigated in the 10.0 - 39.0 GHz region. 10 all-staggered rotameric forms
are possible for this compound. The gas phase consists of a complex
equilibrium mixture of several conformers. Four of these , gAg, gAg', gGg
and gGg', are presumed to predominate. The assignments for one previously
assigned rotamer, gGg, have been extended. The assignments of two "new"
conformers, gAg' and gGg', are reported for the first time. The gAg' rotamer
was found to be the most stable conformer that possesses a dipole moment
different from zero. gAg' is 3.2(4) kJ mol^{-1} more stable than gGg, and 1.8(4)
kJ mol^{-1} more stable than gGg'. In addition to these three rotamers, the gAg
conformer having no dipole moment and hence not observable by microwave
spectroscopy, is assumed to be a fourth stable, low-energy form of the
molecule. The gGg rotamer is stabilised with one weak S-H ••• S
intramolecular hydrogen bond, whereas gGg' is stabilised with two such
bonds. The gAg' conformer displays tunnelling in the ground vibrational state
and in the first excited state of the C-C torsional vibration. The tunnelling is
presumably caused by a concerted rotation by both thiol groups. The
tunnelling frequency is 0.575(80) MHz in the ground vibrational state, and
2.48(5) MHz in the first excited state of the C-C torsion. The microwave
work has been assisted by *ab initio* computations at the HF/6-311++G** and
MP2/6-311G** (frozen core) and B3LYP/6-311++G** levels of theory.

New assignments of hot band transitions of CH_3D in the region 900-1700cm^{-1} and recent results on the analysis of the IR absorption spectrum in the region 1900-3200cm^{-1}

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Infrared spectra of CH_3D in the region 900-1700cm^{-1} have been recorded at temperatures -120 C and 133 C at Giessen. These new spectra have been used together with infrared spectra at room temperature recorded at Kitt Peak for hot band investigations. The Nonad-Triad system has been considered to get new information about the upper states. The preliminary analysis of the IR spectra of CH_3D in the region 1900-3200cm^{-1} has already been reported. Thanks to these new spectra, practically all upper energy levels have been assigned at least for $J, K \leq 10$. More than 5000 ($J \leq 18$) Nonad - Ground State lines have been assigned. Recent improvements achieved for the Nonad and Triad systems will be presented.

OBSERVATION OF NEW INFRARED
TRANSITIONS IN SOLID PARAHYDROGEN

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Following previous FTIR measurements[1,2] in the range $3\,000 - 9\,000$ cm^{-1} we have studied the infrared spectrum of solid parahydrogen at different orthohydrogen impurity levels in the range $10\,000 - 16\,500$ cm^{-1} and in the range $700 - 2\,000$ cm^{-1} .

For the NIR/VIS measurements an internal multireflection cell[1] with 14 cm sample path length was used. Of particular interest here are observations of single molecule transitions of the second overtone band and double transitions of the type $Q_2(J) + Q_1(J')$ $(J, J' = 0, 1)$. At $10\,241.07$ cm^{-1} the new single transition $W_2(0)$ could be observed. The $Q_2(0) + S_2(0)$ double transition near $16\,458$ cm^{-1} exhibits a doublet structure which is explained in terms of resonant hopping of the $J = 2$ roton.

In the MIR region we used a single pass setup with an absorption path length of 4.75 cm. The most important new observations in this region are the $U_0(0) + S_0(0)$ double transition around $1\,520$ cm^{-1} , and the single orthohydrogen transition $U_0(1)$ at $1\,619.12$ cm^{-1} which was previously observed only in normal hydrogen. Furthermore a variety of new double transitions are reported.

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State-to-state energy transfer of electronically excited A $^2A_1$ NH$_2$ observed by time-resolved Fourier transform spectroscopy in the visible

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The state-to-state energy transfer of NH$_2$ in its excited state A $^2A_1$ is observed by time resolved Fourier transform spectroscopy with a very high time resolution of 10 ns. NH$_2$(X $^2B_1$) is produced by photodissociation of NH$_3$ at 193 nm with an excimer laser. About 50 ns after the photodissociation pulse NH$_2$ is excited by a pulsed dye laser from the ground state to high rotational levels (up to J = 21) of the electronic state A $^2A_1$. The time dependent fluorescence is focused into a Fourier transform spectrometer and detected with a photomultiplier and a transient digitizer in slices of 30 ns for about 1 μs after the excitation. The fluorescence of the level excited by the dye laser behaves differently from the fluorescence of the collision satellites. The rotational distributions and the time dependence are presented and the mechanism of the energy transfer is discussed.

THE FIRST DECADE OF THE INTERACTING VIBRATIONAL STATES OF THE $H_2{}^{17}O$ MOLECULE: FIRST OBSERVATION AND THEORETICAL ANALYSIS

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Fourier transform specta of ^{17}O-enriched water vapor between 9500 and 11500 cm^{-1} have been recorded and analyzed for the first time. Precise experimental energy levels have been obtained from the spectrum assignment for (003), (201), (121), (102), and (300) vibrational states with rotational quantum numbers J as high as 9, and K_a as high as 6.

The preliminary theoretical analysis has shown that the scheme of the resonance interactions inside $H_2{}^{17}O$ first decade looks like that for $H_2{}^{18}O$ and $H_2{}^{16}O$ polyads. In particular, the $K_a=0$ energy levels of the (121) state begining from J=7 seem to be perturbed by (070) state formally belonging to the other resonance polyad.

Acknowledgment

OPTOTHERMAL SPECTROSCOPY OF FORMIC ACID DIMER

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For the first time a rotational resolved infrared spectrum of formic acid dimer, $(HCOOH)_2$, was recorded. The spectrum was observed in the region of the carbonyl stretching fundamental (1740 cm^{-1}) with a resolution of 3 MHz using our new molecular beam CO-sideband laser spectrometer with optothermal detection.

Formic acid dimer is one of the most simple cyclic complexes having two hydrogen bonds (binding energy about 50 kJ/mol, 4200 cm^{-1}). It is a prototype molecule for the study of proton transfer which plays an important role in many chemical and biological systems.

We could observe about 600 vibrational-rotational lines of the symmetric and antisymmetric CO-stretch in the dimer which are split by 3 cm^{-1}. The assignment of the lines is in progress and results will be presented at the conference.

LASER VELOCITY MODULATION AND FOURIER TRANSFORM SPECTROSCOPY IN A H₂O/D₂O/He DISCHARGE : OBSERVATION OF THE VISIBLE SYSTEM OF HDO⁺.

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The recent detection of HDO in comets[1] should lead to the future detection of HDO⁺, which is expected to be produced in the gas phase through photoionization of the neutral species, when the comets are in the vicinity of the sun. The observation of the $\widetilde{A}\,^2A_1 - \widetilde{X}\,^2B_1$ visible spectrum of HDO⁺ in the laboratory was therefore attemped by using two experimental approaches.

First a preliminar emission spectrum has been recorded in the short spectral range $16\,400 - 16\,900$ cm⁻¹ and $17\,050 - 17\,300$ cm⁻¹, using a Fourier transform spectrometer Bomem. The species were produced, together with H_2O^+ and D_2O^+ by Penning ionization, generated by active Helium on a vapor produced in a mixture of liquid H_2O/D_2O. On this blended spectrum, the lines of H_2O^+ and D_2O^+ were easily identified by considering the spectra recorded successively from pure H_2O and D_2O respectively

Second, and in order to select the signals from the only ions in the spectral regions of interest, the laser velocity modulation technique was used to record an absorption spectrum between $16\,510$ and $16\,880$ cm⁻¹. The HDO⁺ ions are produced in the positive column of an electrical discharge with a gas mixture of $H_2O/D_2O/He = 0.1/0.1/10$ torr.

By comparison with the spectra recorded in a mixture of H_2O/He and D_2O/He, in emission and in absorption, strong features, only observed in the $H_2O/D_2O/He$, have been tentatively assigned to the vibronic band involving $v_2' = 5, K_a' = 1$, according to the ab initio predictions[2]. The rotational analysis is in progress.

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MAGNETIC SUSCEPTIBILITY AND ELECTRIC QUADRUPOLE MOMENT OF THE $\tilde{A}\,^1A_2$ EXCITED STATE OF H_2CS BY SATURATION DIP AND MODR ZEEMAN SPECTROSCOPY

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We have recently obtained excited-state atomic susceptiblities using two-photon Doppler-free second-order Zeeman spectroscopy in fields up to 5 T [1]. It is the difference of the two level susceptiblities which is actually determined in a transition. The method has now been extended to the bulk susceptibilities, ξ_{gg}, g = a, b, c, of a molecule using laser saturation techniques in high resolution. A complication arises here because the susceptibility anisotropies do also affect the second-order shifts of M-components in a non-spherical system. While the complete tensor is known in the ground state of thioformaldehyde [2], an appropriate anisotropy parameter had to be determined for the $\tilde{A}\,^1A_2$ excited state which was done using microwave optical double resonance (MODR). The upper state bulk value was found to be $\xi^{\tilde{A}} = -(1.28 \pm 0.07)$ MHz T^{-2}, and the anisotropy term to be $\frac{1}{3}(2\xi_{aa} - \xi_{bb} - \xi_{cc})^{\tilde{A}} = -(0.628 \pm 0.008)$ MHz T^{-2} while the corresponding ground state values are [2] $\xi^{\tilde{X}} = -(0.481 \pm 0.045)$ MHz T^{-2} and $\frac{1}{3}(2\xi_{aa} - \xi_{bb} - \xi_{cc})^{\tilde{X}} = (0.437 \pm 0.009)$ MHz T^{-2}. Combining the susceptibilities with the known rotational g-values in the $\tilde{A}$ [3] and $\tilde{X}$ [2] states leads to the electric quadrupole moments $Q_{aa}^{\tilde{A}} = (1.25 \pm 0.53)\ 10^{-39}$ Cm^2 and $Q_{aa}^{\tilde{X}} = (0.93 \pm 0.24)\ 10^{-39}$ Cm^2.

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AIR- AND N$_2$-BROADENING AND SHIFT COEFFICIENTS IN THE ^{12}C^{16}O$_2$ LASER BANDS

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In this paper we report pressure-broadening and pressure-induced line shift coefficients by air and by N$_2$ for 46 rovibrational transitions in each of the two ^{12}C^{16}O$_2$ laser bands, 00^01-$(10^00$-$02^00)_I$ centered at 960.959 cm^{-1} and 00^01-$(10^00$-$02^00)_{II}$ centered at 1063.735 cm^{-1}. High-resolution long-path absorption spectra were recorded at room temperature using the Fourier transform spectrometer at the McMath-Pierce facility of the National Solar Observatory at Kitt Peak. A multispectrum nonlinear least-squares fitting technique[1] was used to determine the broadening and shift cofficients. The air-broadening coefficients obtained in this study agree well with the values in the 1996 HITRAN database;[2] the mean ratios of the present measurements to the HITRAN values are 1.005 for both laser bands. The measured N$_2$-broadening coefficients are 3 to 4 percent larger than the air-broadening values. The pressure-induced line shift coefficients were found to be transition-dependent; different shifts were obtained for P- and R-branch lines having the same J" value. The shift coefficients range from approximately -0.006 to +0.002 cm^{-1} atm^{-1} at 296K, with no noticeable differences between shifts by air and by N$_2$ for the same transition. Our results have been compared with the few available measurements previously reported in the literature.

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LINE POSITIONS, STRENGTHS, AIR-BROADENING, AND AIR PRESSURE-SHIFTS OF THE (0,0) AND (1,0) BANDS OF O_2, $b^1\Sigma_g^+$ - $X^3\Sigma_g^-$

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Line parameters for the A and B bands of gas-phase molecular oxygen have been determined using absorption spectra of zero air at 223 and 283 K recorded by a Bruker IFS 120HR Fourier transform spectrometer (FTS) interfaced to a coolable long pathlength absorption cell (LPAC). A non-linear least squares fitting computer program, written in Interactive Data Language (IDL), was developed to adjust modelled transmittance lines to give the best fit to the observed rovibronic line profiles. Using this software, which incorporated the FTS instrument function and aperture 'self-apodization', up to 31 overlapping O_2 lines were successfully fitted to a total of 96 parameters, including a quadratic baseline. Absolute line positions, air pressure-shifts, linestrengths, and air-broadened widths for 59 individual lines of the A-band, and 51 lines of the B-band, have been calculated. Applications of the data in atmospheric science include determinations of cloud-top height and coverage for atmospheric composition retrievals by the Global Ozone Monitoring Experiment (GOME) on ERS-2, DOAS observations, airglow emission studies, and calculations of shortwave radiative forcing.

The figure below shows air-broadened widths for lines of the O_2 A-band.
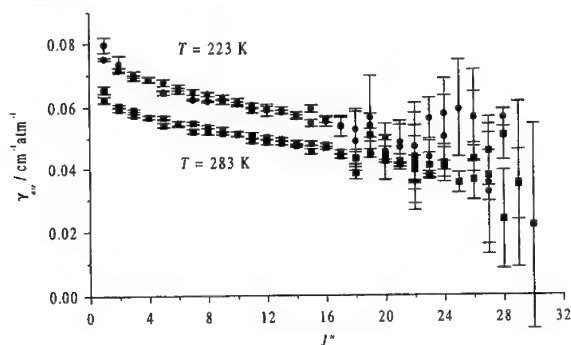
Pressure-Broadening and Pressure-Shifting of
SPECTRAL LINES OF OZONE

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This work is a critical review of experimental and theoretical results on the pressure-broadened halfwidths and pressure-induced line shifts of $^{16}O_3$ absorption lines. A search of the literature revealed some 28 papers on the measurement of pressure-broadened halfwidths for air-, N_2-, O_2-, and self-broadening of ozone, several of these papers also reported measurements of pressure-induced line shifts, and 5 papers on the calculation of pressure-broadened halfwidths for various perturbers. This yields a database for ozone of 4616 experimentally determined halfwidth measurements, 967 transitions for which the temperature dependence of the halfwidth is also reported. The database of calculated ozone halfwidths contains roughly 5000 values, mostly from a single reference, with the temperature dependence of the halfwidth studied for ~140 transitions. Although many data are available, there remains much to be done with regards to the data and accuracy required for practical applications. The collected experimental database is used for intercomparison between different works and to study the influence of the vibrational states, collision partner, and temperature on the broadening. Finally, averaging of the data sets as a function of the rotational quantum numbers (ignoring vibrational dependence) and as a function of vibrational and rotational quantum numbers has allowed the determination of a number of "reliable" values for a number of widely studied lines. The latter should be useful for tests of experimental procedures, remote sensing, and validation of theoretical models. Recommendations for future measurements and calculations to complete these data sets are also made.
Due to the lack of experimental data on pressure-induced line shifts, no systematic comparison could be made. The data are discussed and suggestions for future measurements to aid in the validation of theoretical calculations made.

INVESTIGATION OF J-DEPENDENCE OF LINE BROADENING AND LINESHIFT COEFFICIENTS IN THE $v_1 + 3v_3$ BAND OF ACETYLENE

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Line broadening coefficients γ and line shift coefficients δv have been measured for 10 lines of the $v_1 + 3v_3$ band of acetylene in the P and R branches, the rotational quantum number J" ranging from 1 to 17. The absorption cell was a multi-pass Herriot cell with an optical length of about 35 m. The laser radiation was produced by a tunable cw semiconductor laser diode system providing about 20 mW power at the entrance window of the cell. A single scan extended over a range of 0.8 cm^{-1}. A Voigt profile was fitted to the observed line shape.

Up to now, self-broadening and broadening by N_2 and Ar perturbers have been investigated, but experiments studying the effect of other rare gas perturbers, of O_2 and of air are presently in progress. The knowledge of broadening coefficients in air of atomospheric pressure is an important prerequisite for a reliable detection of small amounts of pollutants in air.

Some of our results are compiled in Table 1. The values of γ show a

	γ_{self}	δv_{self}	γ_{N_2}	δv_{N_2}
R(1)	0.384(10)	-0.0052(20)	0.215(10)	-0.0085(30)
R(15)	0.266(10)	-0.0185(25)	0.152(10)	-0.0167(30)

.Table 1: Lineshift δv and line broadening γ in cm^{-1}/bar for two lines of the $v_1 + 3v_3$ band of acetylene

continuous decrease with increasing J", whereas the lineshifts show the opposite behaviour, but are distinctly smaller. Our results are in good agreement with previous data [1] obtained for selected lines of the $v_1 + 3v_3$ band.

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MONOFLUOROOXIRANE: SYNTHESIS, HIGH RESOLUTION SPECTROSCOPY, STRUCTURE, IR LASER CHEMICAL REACTION DYNAMICS AND AB INITIO CALCULATIONS

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Recently, we have reported the first synthesis of the chiral monofluorooxirane and its doubly deuterated isotopomer [1]. We have rotationally analyzed the high resolution infrared spectra of ν_{11}, ν_{12} of the undeuterated and ν_7, ν_9 of the deuterated oxirane on our BOMEM DA002 interferometric FTIR spectrometer. This provides one of the very few examples of a rotational analysis for chiral compounds, which is of crucial importance for fundamental reaction dynamics and symmetry violation studies of chiral molecules [2]. The rotational analysis provides an approximate r_0 structure to be compared with results obtained by ab initio calculations. We have furthermore investigated the IR–multiphoton excitation, and dissociation of the fluorooxiranes:

$$D_2C\!-\!\!-\!\!-\!CHF \quad \begin{array}{c} \xrightarrow[\bar{\nu}\,=\,1083\mathrm{cm}^{-1}]{24\,\cdot\,h\nu} \quad D_2C\!=\!C\!=\!O\,+\,HF \\[2mm] \xrightarrow[\bar{\nu}\,=\,1083\mathrm{cm}^{-1}]{24\,\cdot\,h\nu} \quad HDC\!=\!C\!=\!O\,+\,DF \end{array} \quad \frac{\alpha\alpha}{\alpha\beta}\simeq\frac{2}{1}$$
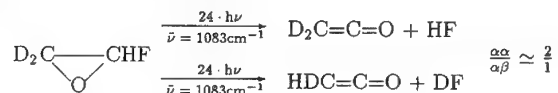
The complete reaction dynamics has also been calculated ab initio [3], including possible reaction mechanisms, yields, and HF/DF branching ratios. The theoretical results are compared to the predictions of a simple structure–reactivity relationship, obtained from the approximate r_0 structure of the fluorooxirane.

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ABSOLUTE LINE INTENSITIES IN THE ν_3 FUNDAMENTAL
BAND
OF CARBON DISULFIDE CS_2.

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The ν_3 fundamental band of CS_2 is a very intense band and is situated in the region of 1500 cm^{-1}. It is important to measure the absolute line intensities for this band which is used for calibration of other spectra[1]. Furthermore, this molecule is also found in the earth atmosphere, constituting one of the major sources of OCS^2.

Using a tunable diode-laser spectrometer, we have carefully recorded several individual absorption lines belonging to the ν_3 band in the spectral range of 1500 cm^{-1}. These lines were selected over a wide range of J quantum number and we have deduced the experimental strengths parameters by using the equivalent width method.

From these data, we have determined by least squares fitting the vibrational band strength S_v^0 at 297 K. The first Herman-Wallis coefficient was found very small

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CORRELATED AND NON-CORRELATED LINESHAPE MODELS
UNDER SMALL LINE SHIFT CONDITION.
APPLICATION TO SELF-PERTURBED CH₃D

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Seven ro-vibrational lines in the ν_3 band of self-perturbed CH₃D
have been measured, in the infrared region 1200-1300 cm⁻¹. The high
resolution and high S/N ratio, provided by the diode-laser spectrometer,
have made possible the analysis of their lineshape with phenomenological
profiles including the rotational relaxation and the Doppler effect with a
pressure-confinement of the active molecule. The lineshape fitting method
permits to deduce the line intensity S (cm⁻²), the collisional broadening
γ_c (cm⁻¹) and the narrowing parameter ν_{vc} (cm⁻¹) in the non-correlated
hypothesis, or the parameter ν_{vcd} (cm⁻¹) in the correlated hypothesis. For
this system, at this pressure regime, the collisional spectral line shift δ_c
(cm⁻¹) can be neglected, so that it appears that the two lineshapes are
virtually identical and verify a simple relation $\gamma_c + \nu_{vc} \approx \nu_{vcd}$. However to
obtain this result, it is necessary to re-formulate the soft-collision profile
proposed by Varghese et al.[1]. Then the two limiting cases, soft and hard-
collision models[2], may be used indifferently and describe the shape of the
lines satisfactorily. As a result the linestrength and the self-broadening
coefficients are determined with accuracy and are compared with theoretical
calculations. A nearly constant value of the velocity-changing parameter
is obtained, quite close to the dynamical friction parameter $\beta_c^0 = 0.037$
cm⁻¹ atm⁻¹.

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INVARIANT PARAMETERS FOR C_{3v} MOLECULES IN THE TENSORIAL FORMALISM

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Invariant parameters defined as combinations of spectroscopic parameters independent of a spectroscopic model are considered[1]. The algorithm for construction of invariant parameters will be discussed using the representation of rovibrational operators described in Ref[2]. The validity of the method was tested for the triad of interacting vibrational states of CH_3D. The practical advantage of invariant parameters is that they allow to avoid ambiguities and to introduce a physically meaningful set of spectroscopic constants. They can also be used for a comparison of various models of the effective Hamiltonian. The comparison with similar polyads of CH_4 shows that the number of linear invariant parameters decrease with decreasing symmetry of a molecule.

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H_3^+ at Dissociation: Potential Energy Surface and Spectroscopy

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We have constructed [1] a global two-valued ground-state potential for H_3^+ molecule. The energy switching approach is used to combine different functional forms for three different energy regimes. The Born-Oppenheimer surface of Dinelli et al. [2] is used for energies up to 20000 cm^{-1}, for higher energies the many-body expansion of Sorbie and Murrell [3] is fitted to *ab initio* calculations [4], at large separations long-range terms are combined with accurate diatomic potentials. This produces an accurate global potential which represents all aspects of ground state H_3^+ including the avoided crossing of the two surfaces and dissociation limits. This surface is suitable for studying spectroscopy, high-lying bound states and reaction dynamics.

At present we are performing full 3D quantum calculations, for both $J=0$ and non-zero total angular momentum. We note that our potential, unlike ones used for previous studies in the dissociation region, correctly represents the attractive long range effects. This will undoubtedly lead to extra, extended vibrational states with consequent difficulty in performing reliable calculations. Results will be presented at the conference.

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LINE STRENGTHS OF TORSION-ROTATION TRANSITIONS OF METHANOL FOR $J \leq 20$ AND $v_t \leq 1$, INCLUDING TORSIONAL VARIATION OF THE DIPOLE MOMENT OPERATOR

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There are two aspects to the torsional variation of the dipole moment operator μ. The first can be thought of as the variation which would be obtained from *ab initio* calculations carried out at various torsional angles. The second can be thought of as the (trivial, but potentially confusing) variation which arises from internal rotations of various parts of the molecule in the PAM, RAM or IAM axis systems used to treat the methyl rotor problem. In the first half of the poster we present line strength calculations carried out using a dipole moment operator obtained by combining experimental values for the μ_a and μ_b permanent dipole moment components with *ab initio* generated[1] periodically varying contributions to μ_a, μ_b and μ_c, and using torsion-rotation wavefunctions obtained from the latest large global fit to experimental torsion-rotation transitions[2]. We present a table which analyses the contributions to the line strengths from each of the μ-components. In the second half of the poster we discuss the reasons why $\Delta v_t = \pm 1$ torsional transitions are "caused" by the μ_a and μ_b components of the permanent dipole moment in the PAM and RAM axis systems, but are caused by the derivative with respect to torsional angle of the μ_c component in the IAM axis system.

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Space Groups, Site Symmetry, Large-Amplitude Motions and Effective Rotational Hamiltonians

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Molecular symmetry groups of some molecules with two or three periodic large-amplitude motions (dimethylether, inverting dimethylamine, butane, trimethylboron, acetylacetone and others) are investigated. The unit cells of these models are equivalent with those of known two- and three-dimensional space groups. In the space groups of crystals, the end points of the allowed k-vectors characterizing many physical properties cover the complete volume of the Brillouin zone. In contrast, only a few k- (or σ-) vectors are allowed for molecules with periodic large-amplitude motions.

Atoms, molecules or ions may occupy sites with different site symmetries within the same unit cell of a crystal, and their properties depend not only on the unit cell but also on the specific site. In a similar manner, effective rotational Hamiltonians for molecules with periodic large-amplitude motions[1,2] depend not only on the molecular symmetry group but also on the specific site. Examples of such Hamiltonians are given for dimethylether, dimethylamine, *trans-* and *gauche*-butane, acetylacetone and others.

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A theoretical study of the hydrogen cyanide dimer

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The hydrogen cyanide dimer is one of the few hydrogen–bonded complexes for which rotationally resolved overtone spectroscopy has been performed. Published work [1] concerns the first overtone of the unbound CH stretching vibration $2\nu_1$ which behaves similarly to free HCN and is red–shifted by only 6.318 cm^{-1}. The more interesting combination tone $\nu_1 + \nu_2$ was observed recently by Scoles and coworkers [2]. The first overtone of the bound CH stretching vibration $2\nu_2$ has not yet been found.

On the basis of ab initio calculations within the coupled electron pair approximation (CEPA) and the coupled cluster method perturbatively accounting for connected triple substitutions (CCSD(T)), a five–dimensional potential energy surface was constructed for the stretching vibrations of (HCN)$_2$. The equilibrium dissociation energy is $D_e = 19.7$ kJ/mol and the electric dipole moment $\mu_e = 6.68$ D. We predict the band origin of the $2\nu_2$ band to be 6370 cm^{-1} with a transition moment of 0.0028 D. The transition moments of the $2\nu_1$ and $\nu_1 + \nu_2$ bands are 0.0094 and 0.0019 D, respectively.

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INFRARED DIODE LASER ABSORPTION SPECTROSCOPY OF BOUND AND QUASIBOUND STATES OF HeH+

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Infrared diode laser absorption spectroscopy has been used to record the pure rotational and vibration rotational transitions of ^{4}HeH$^+$ near its dissociation limit. HeH$^+$ was generated in an air cooled H_2/He discharge and detected by velocity modulation. Thirty five pure rotational transitions, including three quasibound to quasibound (Q-Q) and three bound to quasibound (B-Q) transitions in the v= 0,1 and 2 states and ten new vibration rotational transitions, arising from both low (v=1,2) and high (v = 4–7) vibrational states, have been measured. The highest quasibound level involved in the spectrum (v=0, $J = 26$) is about 2000 cm^{-1} higher than the dissociation limit. The measured transition frequencies are in very good agreement with *ab initio* calculations based on the form of the adiabatic potential model developed by Fournier and Richard[1]. One Q-Q transition, v = 0, $J = 26\leftarrow25$, was measured to have larger linewidth than others due to rotational predissociation of its upper level (v=0, J =26).

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On the Spin-Orbit Interactions between the Low-Lying $^2\Pi_g$ and $^2\Sigma_g^+$ electronic states of $CuCl_2$

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Abnormally large e-f separations have been observed in the (v_1, 0, v_3) levels of the ground $X^2\Pi_{g(3/2)}$ state of $CuCl_2$ about 2500 cm^{-1} above the lowest vibrational level (0,0,0). The largest splittings are accompanied by extra lines in the dispersed fluorescence spectra. Some of the extra lines have resolvable Cu hyperfine structure; they are assigned as transitions to levels which result from mixing essentially between $^2\Pi_g$ and a nearby $^2\Sigma_g^+$ state.

We have used an effective Hamiltonian to model the $^2\Pi \sim {}^2\Sigma$ interaction and derived molecular constants for the unknown $^2\Sigma$ state using a non-linear least-squares fitting routine. Taking an arbitrary value of the spin-orbit parameter A_Π of -300 cm^{-1}, we estimate the $^2\Sigma_g^+$ state to lie around 3000 cm^{-1} above the (0,0,0) level of the $X^2\Pi_{g(3/2)}$ ground state.

The ν_1, $2\nu_2$, $2\nu_3 + \nu_4$ Band System of Carbonyl Fluoride

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The infrared spectrum of carbonyl fluoride, COF_2, has been measured in the region 1880 cm^{-1} to 1980 cm^{-1} using a Bruker Fourier Transform Spectrometer at 0.003 cm^{-1} resolution and Diode Laser spectroscopy at Doppler limited resolution . In this region the ν_1 band at 1945 cm^{-1} dominates the spectrum and is in Fermi resonance with the $2\nu_2$ band at 1914 cm^{-1} and in B-type Coriolis resonance with the $2\nu_3 + \nu_4$ band at 1936 cm^{-1}. 1220 lines from the ν_1 and $2\nu_2$ bands were successfully fitted using an S-type Watson Hamiltonian in the III^l representation giving an obs-calc RMS of 0.0006 cm^{-1}.

The absorption coefficients of this band system have also been determined using a Bomem Fourier Transform Spectrometer under 0.005 cm^{-1} resolution at a gas pressure of 3.2 Torr, 10cm pathlength and at room and stratospheric ($\sim$ 200 K) temperatures and the integrated intensity in this region is found to be 3.07×10^{-17} cm/molecule at room temperature and 3.26×10^{-17} cm/molecule at $\sim$200K. Using calculated spectra the integrated intensities were predicted to be 2.90×10^{-17} cm/molecule and 3.01×10^{-17} cm/molecule respectively using transition dipole moments of 0.1592 Debye for ν_1 and 0.1097 Debye for $2\nu_2$. The small discrepancy in integrated intensity can be accounted for from thermally populated states, whose contribution was not calculated.

THE HYPERFINE STRUCTURE OF AsF$_3$
IN THE VIBRATIONAL STATE v$_4$=1

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In 1996 we published the observation of direct ℓ-type resonance transitions of AsF$_3$ in the vibrational state v$_4$=1 measured in Kiel by means of microwave Fourier transform spectroscopy[1]. The transitions showed splittings due to the arsenic nuclear quadrupole coupling but only the central frequencies of the transitions were reported and analysed together with data obtained in the millimeter and infrared range. The data were fitted using two reduced forms of the effective Hamiltonian and the unitary equivalence of the parameter sets as introduced in Ref.[2] was demonstrated. First attempts to analyse the hyperfine structure of the transitions clearly showed that resonances visible in the rovibrational spectrum also affect significantly the hyperfine structure. This allowed to verify that the two choices of reduction can also be used for the fit of the hyperfine data. Theoretical relations between the hyperfine parameters of both sets have been derived and compared with the results obtained from the analysis.

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High Resolution Spectroscopy of Ar–CH$_4$ and Kr–CH$_4$ in the 7 μm Region
($j = 1 \leftarrow 0$ and $j = 0 \leftarrow 1$ transitions)

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The absorption spectra of Ar–CH$_4$ and Kr–CH$_4$ van der Waals complexes were observed in the 7 μm region. The complexes were produced in a pulsed slit jet and detected by a tunable diode laser spectrometer. The allowed transitions from the three $^R P_0$, $^R Q_0$ and $^Q R_0$ branches, which correspond to the $j = 1 \leftarrow 0$ transition of the CH$_4$ part inside the complexes, were measured for both Ar–CH$_4$ and Kr–CH$_4$ complexes close the $R(0)$ line of the ν_4 fundamental band of methane. Additionally, several weaker nearly forbidden low J transitions from the $^Q P_0$ and $^R R_0$ were found, enabling an unambigious determination of the rotational and centrifugal distortion constants for the $j = 0$ level of the ground vibrational state of the complexes. We have further recorded and assigned the allowed transitions from the $^P Q_1$, $^Q P_0$ and $^P R_1$ branches, corresponding to the $j = 0 \leftarrow 1$ transition in the region close to the $P(1)$ line of methane.
The spectroscopical analysis of the recorded transitions is in progress and the results will be presented on the conference.

Microwave spectroscopy of CFC-Halon replacement compounds:
Bromodifluoromathane and 1-bromo-1-fluoroethane

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Chlorine and bromine have been implicated in a massive depletion of
stratospheric ozone over Antarctica. As the source of those halogens is
anthropogenic emission of haloalkanes, they have been forced to consider
urgently possible replacements for conventional halocarbons. Before a
massive emission of these replacements compounds into the atmosphere,
their detailed spectroscopic constants should be necessary for the eventual
monitoring and in the modeling of ozone depletion and global warming. We
have, therefore, investigated the microwave spectra of $CBrF_2H$ and $CBrFH-CH_3$ which are possible replacements of a fire extinguisher Halon .

The samples of $CBrF_2H$ was purchased from PCR Incorporated and
$CBrFH-CH_3$ was synthesized from $CHF=CH_2$ and HBr. The moments of
inertia of bromodifluoromathane and 1-Bromo-1-fluoroethane are almost the
same, because of the very close moments of inertia of the C-F and the $C-CH_3$
groups. The microwave spectra of $CBrF_2H$ and CBrFH-CH3 for the $^{79/81}Br$
species have been measured by a conventional Stark modulation
spectrometer, leading to the rotational, centrifugal distortion, and the
bromine nuclear quadrupole coupling constants. The dipole moments of
$CBrF_2H$ is almost parallel to the c-axis and that of $CBrFH-CH_3$ lies mainly
on the b-axis and slightly on the a-axis. For $CBrF_2H$ and CBrFH-CH

MICROWAVE SPECTRUM. RING PUCKERING VIBRATION AND AB INITIO CALCULATIONS ON 1,1-DIFLUOROCYCLOBUTANE

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The rotational spectrum of 1,1-difluorocyclobutane has been investigated in the centimeter (8-40 GHz) and millimeter-wave regions (96-106 and 144-159 GHz). Analysis of the spectra for the $v_p=0/1$ and $v_p=2/3$ ring puckering vibrational states has been carried out using two-states Hamiltonians, yielding accurate rotational and centrifugal distortion constants, coupling parameters and the energy spacings ΔE_{01} and ΔE_{23}. The spectrum for the $v_p=4$ to $v_p=6$ ring puckering states was satisfactorily accounted for in terms of an effective semirigid Hamiltonian for each vibrational state. A reduced potential function for the ring puckering vibration has been obtained from the observed vibrational variation of the rotational constants and the energy spacings ΔE_{01} and ΔE_{23}. The calculated variation of the quartic centrifugal distortion constants with the ring puckering quantum number reproduces satisfactorily the experimental trends. Ab initio calculations at RMP2 6-31G(d) and RMP2 6-31G(d,p) levels have been carried out for this molecule, comparing the experimental and ab initio potential functions, coupling terms and ring puckering dynamical parameters. Finally, an ab initio near equilibrium structure is presented.

The Molecular Geometry and Hyperfine Coupling Constants of OPF

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Free gas phase OPF has been prepared for the first time by passing an electric discharge through a mixture of PF_3 and O_2, and the microwave spectra of two isotopomers have been measured in the 4-26 GHz frequency range. These transitions were analysed in terms of rotational, centrifugal distortion, and spin-rotation coupling constants. The determined rotational constants have been used to calculated r_0, r_z, and approximate r_e molecular geometries, and the spin-rotation coupling constants have been used to calculate the nuclear shielding parameters of the fluorine and phosphorus nuclei. Because both F and P are spin $\frac{1}{2}$ nuclei, and because both sets of determined spin-rotation coupling constants had very similar values, assignment of these constants to a particular nucleus was not possible; the nuclear shielding parameters of this species have been calculated using both possible assignments.

Microwave Spectra of Ethylene Glycol and the Identification of the gGg´-Conformation

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Refinement of the ab initio Models[1] for Ethylene Glycol in the g´Ga- and gGg´-conformations by fitting to experimental rotational constants[2] has guided the way to the identification of a second hydrogen bonded conformation for the main species of Ethylene Glycol.

Spectra have been recorded as Molecular Beam Fourier Transform Spectra[3], as Stark Spectra[4] and with the Double Resonance Technique[5].

So far only parity conserving μ_b-transitions have been identified (11 each for the 0^+- and 0^--species), but it is expected that parity breaking μ_a- and μ_c-transitions will be assigned in time for the meeting.

Preliminary rotational constants for the gGg´-conformation of Ethylene Glycol are:

A : 15213.6 MHz,   B : 5538.3 MHz,   C : 4594.3 MHz.

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HIGH RESOLUTION STIMULATED RAMAN SPECTRUM OF THE ν_2 BAND OF DIACETYLENE AND ASSOCIATED HOT BANDS.

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The Raman spectrum of the ν_2 band of C_4H_2 has been recorded at near Doppler Resolution using the quasi-cw Inverse Raman Spectrometer of Madrid[1]. The region between 2180 and 2190 cm^{-1} was recorded, including the Q branch of the fundamental band along with that of hot bands originating in the ν_9, $2\nu_9^0$, $2\nu_9^2$ and ν_7 states. The spectrum of the fundamental shows strong perturbations.

Progress in the analysis of these bands will be reported.

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THE HIGH RESOLUTION INFRARED SPECTRUM OF C_6D_6

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The gas phase infrared spectrum of C_6D_6 has been recorded between 400 and 4000 cm^{-1} at the resolution of 0.008 cm^{-1}, on a *BOMEM DA2* interferometer using a multipass cell with a 6 m path-length. We are analysing the parallel type fundamental and combination bands of the spectrum to determine the wavenumber of fundamentals with higher accuracy and the anharmonic constants. This analysis is allowed by means of the ab initio quartic force field calculated by a finite difference numerical method. The wavenumbers of the Q-branches of the hot bands accompanying as satellites the IR bands depend on the anharmonic constants x_{ij}, g_{ij} and on the vibrational l doubling constants R_{ij} and S_{ij}. Here we present the preliminary results of the analysis.

SATURATION SPECTRUM OF THE The v_2 / v_4 DYAD OF AsH₃

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The v_2 / v_4, dyad of arsine, AsH₃ , has been investigated between 875 cm⁻¹ and 1100 cm⁻¹ by laser sideband spectroscopy. In total 189 transitions, including four perturbation allowed transitions with $\Delta(k - \ell) = 3$, have been observed with sub Doppler resolution. Saturation of dipole forbidden transitions have not been reported yet for the AsH₃ molecule Quadrupole hyperfine structure as well as vibration-rotation splitting of $|k - \ell| = 3N$ levels in both fundamental bands have been analysed. Together with MW and RF data (241 frequencies) reported in the literature, a total of 884 transition frequencies was used to fit 16 ground state parameters and 58 excited state parameters of the v_2 / v_4 dyad. The standard deviation of the fit is 150 kHz. The spectrum of arsine can now be calculated in the range from 750 cm⁻¹ to 1150 cm⁻¹ with comparable accuracy and makes it suitable to serve as a secondary frequency standard.

LOCALISATION OF VIBRATIONAL ENERGY IN ^{120}SnD$_4$

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High resolution FTIR spectra of the stretching fundamentals as well as the first and second stretching vibrational overtones of deuterated stannane have been rotationally analysed. The results indicate a surprisingly similar behaviour of deuterated stannane (^{120}SnD$_4$) and normal stannane (^{116}SnH$_4$). Vibrational energy localisation with almost degenerate local mode states $[n000A_1]$ and $[n000F_2]$ takes place in the the second stretching vibrational overtone in both molecules. Consequently, the dynamical symmetry of the molecule changes from that of a spherical top to a prolate symmetric top. This can be seen looking at the high resolution FTIR spectra of the second stretching vibrational overtone, where the symmetric top K-structure of a prolate symmetric rotor is observed.

ABSOLUTE INTENSITY MEASUREMENTS
IN THE 7.5 μm REGION OF ACETYLENE

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Spectra of C_2H_2 have been recorded at room temperature in the range from 1140 to 1490 cm^{-1} using a Bruker IFS120HR spectrometer. Sample pressure/absorption path length products ranging from 1.3 to 330 hPa×cm have been used. Absolute line intensity measurements have been performed in the $v_4 + v_5$ cold band and in hot bands involving the bending modes v_4 and v_5.[1] The potential influence of resonances between the levels on the overall intensity of the bands and on the intensity distribution of the rotational lines within these bands is studied. Results will be presented and discussed.

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HIGH RESOLUTION NIR DIODE LASER SPECTROSCOPY OF PROPYNE

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The $3\nu_1+\nu_3+\nu_5$ band of propyne centered at 12760 cm^{-1} has previously been investigated by photoacoustic spectroscopy [1] with 0.01 cm^{-1} accuracy, and within a supersonic jet [2]. We have constructed a laser diode spectrometer stabilised to and tracked by a scanning Fabry-Perot étalon which reproduces test spectral lines of water to 0.0003 cm^{-1} precision, well below the Doppler width. At this resolution rotational structure within P, R and Q branches of the propyne $3\nu_1+\nu_3+\nu_5$ band becomes visible, and has been modelled and analysed using a Hamiltonian containing centrifugal distortion and pure rotation terms. Parameters for this and the overlapping $3\nu_1+\nu_3+\nu_5+\nu_{10}-\nu_{10}$ hot band are presented.

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DIODE LASER SPECTROSCOPY OF
CIS-1-CHLORO-2-FLUOROETHYLENE IN THE ν_6 BAND REGION

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Cis-1-chloro-2-fluoroethylene has been synthesized, and gas-phase infrared spectrum has been investigated in the ν_6 band region around 1062 cm^{-1}, at Doppler limited resolution, using a tunable diode laser spectrometer. The measurements were performed at 240 K in order to minimize hot band contributions.

This compound is a planar molecule belonging to the C_s point group and the ν_6 vibration of symmetry species A', approximately representing the C-F stretching mode, yields an a/b-hybrid absorption. Since the asymmetry parameter κ is -0.895, this molecule approaches to a prolate symmetric top and the structure exhibits patterns characteristic of parallel (a-type) and perpendicular (b-type) bands.

The band centre is characterized by a series of $^Q Q_K$ subbranches showing a packed J structure. Valuable information for the analysis of the spectrum are mostly provided from rotational details of P and R branches. An observation coming from subband analysis concerns the presence of interactions, whose effects should arise from Coriolis resonance with $\nu_9+\nu_{10}$ vibration (A") lying around 1062 cm^{-1}.

Using the Watson's A-reduction Hamiltonian in the F representation, the identified transitions led to the determination of accurate spectroscopic parameters for the ν_6 band of the ^{35}Cl species of Cis-CHF=CHCl. Spectra, details of the interpretation, and results obtained from the analysis will be presented.

VIBRATIONAL PREDISSOCIATION IN THE VIBRONIC STATES OF ANILINE-NEON Van der WAALS COMPLEX: HIGH RESOLUTION LASER SPECTROSCOPY AND DISPERSED FLUORESCENCE

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The study of intramolecular dynamics is of importance in many respects for the understanding of chemical reactions. Van der Waals complexes offer a convenient model situation, in which the ability to choose the partner allows to tune the position and the number of available states participating in the evolution of the initially prepared state. We report about two independent sets of experimental spectroscopic data which both contain information on the vibrational dynamics occuring in the aniline-neon Van der Waals complex in its S_1 electronically excited state.

The high resolution LIF spectra of the three vibronic bands of the $S_1 \leftarrow S_0$ transition investigated in this complex, $6 a_0^1$, I_0^2 and I_0^1 , exhibit lifetime broadening with respect to the corresponding states in the aniline monomer, while the 0_0^0 band shows the same linewidth for both the monomer and the complex. The dispersed emission spectra taken under excitation of the same three vibronic bands give access to both the final aniline monomer states distribution in the vibrational predissociation of this complex and to the rates at which this dynamics proceeds. The overall results are discussed in a consistent way, with emphasis being given to the role of the coupling between the intramolecular and the intermolecular vibrational states.

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COLLISIONAL COUPLING BETWEEN THE STARK COMPONENTS OF CH_3F ROTATIONAL TRANSITIONS

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By studying the spectrum of methylfluoride in an electric field, the well resolved Stark components were observed[1] to have pressure broadening coefficients different from each other and larger than what measured on the unresolved line in absence of electric field. This was explained in terms of collisional coupling, an effect arising when coherent amplitude transfer between overlapping lines produces a collisional lineshape different from the simple superimposition of their lorentzian shapes.

We present here a lineshape study performed at intermediate fields, when the Stark components are neither well resolved nor completely overlapped. This allows us to observe collisional coupling under particularly favorable conditions. Indeed, the ratio distance between lines / linewidth, which is the crucial parameter, can be modified not only by changing the gas density, as in the usual collisional coupling studies, but also by tuning the external field, which in our case sets the frequency separation between the lines.

By comparing the observed lineshapes to theoretical predictions, we could perform a detailed check of the models proposed for the calculation of the off-diagonal relaxation matrix and for the diagonalization of the time evolution operator in the Liouville space of the lines.

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VIBRATIONAL AND ROTATIONAL STRUCTURE OF THE GROUND STATE OF THE CS_2 MOLECULE AT HIGH ENERGIES

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A dispersed fluorescence spectrum of CS_2 has been recorded over a wide wavelength range (from 4350 to 10200 Å). The observed transitions correspond to 152 vibrational levels, situated in the electronic ground state between 5600 to 18700 cm^{-1}. Fluorescence was excited by an UV argon ion laser in the R system at 351.1 nm in the same manner as used by Bernath et al [1]. The relatively broad argon ion laser line is situated in a band head, and thus due to the simultaneous excitation of multiple rotational lines, we also obtained information about the rotational constants of the different vibrational levels.

Statistical studies of a complete spectrum [2] have shown that the vibrational spectrum of CS_2 shows a transition to chaotic behavior at about 13000 cm^{-1}. However, in our case, only a sparse ensemble of levels has been observed. Thus it was possible to recognize regular progressions up to high energy (16000 cm^{-1}) and to reproduce these levels by an integrable Hamiltonian that takes into account the 1:2 Fermi resonance. Some other vibrational levels could not as yet be identified; their appearance is probably due to a strong mixing with the asymmetric stretch v_3.

The last vibrational level observed by infrared spectroscopy is situated at 6462 cm^{-1} [3]. Beyond this limit, no systematic information about rotation was available before this work. In addition to the vibrational fit, we studied, for the first time, the dependence of the rotational constant B_v on vibrational excitation for energies up to 16000 cm^{-1}.

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ROTATIONAL SPECTRA OF CH$_2$I$_2$ AND CD$_2$I$_2$

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The analysis of the rotational spectrum of methylene iodide has for a long time been prohibited by the complex hyperfine structure and rich satellite patterns associated with the low frequency $\angle ICI$ bending mode. Only recently, combined results from supersonic jet and room-temperature broadband mm-wave spectroscopy allowed determination of the ground state rotational and hyperfine coupling constants for CH$_2$I$_2$[1], and CD$_2$I$_2$[2] and the molecular structure of methylene iodide were derived.

We have presently extended the analysis of the broadband mm-wave spectra of methylene iodide, recorded with the BWO-based spectrometer in Warsaw, to the excited states of the $\angle ICI$ bending mode. The vibrational frequency of the mode is estimated to be near 100 cm^{-1} and its satellite progression has been assigned up to $v = 4$. Transition frequencies of many ^{b}R- and ^{b}Q-type transitions have been measured for J up to 200, and sextic level spectroscopic constants have been determined. The rich room-.temperature mm-wave spectra of both CH$_2$I$_2$ and CD$_2$I$_2$ are now well understood and examples of the assigned broadband spectra and preliminary spectroscopic constants are presented. The changes in both rotational and centrifugal constants show relatively small anharmonicity, in line with anticipation for a mode for which low vibrational frequency is primarily the result of a mass effect rather than of a particularly low force constant.

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SPECTROSCOPY OF JET COOLED COMPLEXES
BETWEEN CHIRAL MOLECULES :
A NEW METHOD FOR ENANTIOMERIC DISCRIMINATION

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Chiral recognition, a process of fundamental interest in chemistry and biology, usually takes place through weak stereochemical interactions in diastereoisomeric contact pairs.

The formation of weakly bound complexes in a supersonic expansion and their characterization by means of laser fluorescence excitation techniques provides a yet unexplored method to differentiate between enantiomers and investigate the nature of intermolecular forces involved in the chiral discrimination on the microscopic point of view.

By using 2-naphthyl-1-ethanol as a optically active chromophore, we have studied the effect of complexation with a series of non chiral and chiral aliphatic alcohols on its photophysical properties (microscopic solvent shift, formation of conformers and fluorescence decays). In the case of pure enantiomeric pairs, the fluorescence excitation spectra show that the shifts of the S_0-S_1 transition are specific of the homo and hetero chiral pairs and allow them to be clearly distinguished in a racemic mixture. Ground state depletion experiments (hole burning spectra) show that the chiral discrimination is sensitive to the conformation of the complexing agent since for each diastereoisomer two conformers have been identified. The fluorescence lifetimes following selective excitation of alcoholic complexes are longer than those of the uncomplexed molecule and also depend on the particular diastereoisomer excited.

Parallel theoretical calculations on the structure and binding energy of the complexes by exchange perturbation methods have been used to understand the nature of intermolecular forces responsible for the chiral discrimination.

NUCLEAR SPIN CONVERSION IN MOLECULES AND HIGH RESOLUTION SPECTROSCOPY

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Nuclear spin isomers of molecules (a familiar example is the ortho and para H_2) form the territory which is well–known to exist but remains almost unexplored. This happened because of the lack of practical methods to separate spin isomers of molecules heavier than hydrogen. Presently such methods start to appear, which opens up the new fields of research.

In this report we review the conversion of CH_3F nuclear spin isomers (ortho–para conversion) and discuss the relation between the nuclear spin conversion in molecules and high resolution spectroscopy. The ground for this relation is the specific mechanism behind the nuclear spin conversion which is based on the *intramolecular* mixing of spin states by hyperfine interactions. This new type of relaxation can be called *quantum relaxation*[1].

The recent observation of the level–crossing resonances in CH_3F nuclear spin conversion[2] has made this relation even closer. A homogeneous electric field produces splitting and crossings of the molecular rotational levels, which dramatically increases the conversion rate. Scanning of the electric field gives the level–crossing spectra of the spin conversion rate. This new type of high resolution spectroscopy promises to provide reach information on the ortho–para mixing in molecules. We discuss the role in these spectra the spin–spin and the spin–rotation interactions, the molecular inversion and the Pauli symmetrisation of the molecular quantum states.

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Q1

ROTATIONAL SPECTRA OF THE TETRAHYDROTIOPHENE ·· HCl AND TETRAHYDROTIOPHENE ·· HF DIMERS

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The ground state rotational spectra of the dimers formed between HCl and HF with tetrahydrotiophene (THT, C_4H_8S) have been measured in the frequency range 6-18.5 GHz using a molecular beam Fourier transform microwave spectrometer.

The spectra of several isotopic species of the dimer THT···HCl ($C_4H_8{}^{32}S···H^{35}Cl$, $C_4H_8{}^{34}S···H^{35}Cl$, $C_4H_8{}^{32}S···H^{37}Cl$, $C_4H_8{}^{32}S···D^{35}Cl$ and $C_4H_8{}^{32}S···D^{37}Cl$) have been observed. Spectral analysis gave rotational, quartic centrifugal distortion and Cl-nuclear quadrupole coupling constants for each isotopomer. For the THT···HF dimer, the D_{aa} H,F nuclear spin-nuclear spin coupling constant has also been determined.

For both complexes the spectroscopic constants have been interpreted in terms of geometries in which a non linear hydrogen bond is formed by the hydrogen halide with the sulfur atom of THT. The hydrogen halide lies on the plane bisector to the CSC angle of THT with a pyramidal arrangement at S.

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Q2

A NEW HETERODYNE SPECTROMETER WITH TUNABLE DIODE LASERS : ATMOSPHERIC OZONE SPECTRA NEAR 1120cm^{-1}

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Heterodyne spectrometry is a potentially powerful technique for astronomical or geophysical investigations. An heterodyne receiver works by mixing the radiation under study with the laser radiation from a local oscillator on a fast photodetector. In the infrared, CO_2 lasers allow to reach the detection limits, but such systems with fixed local oscillator have limited spectral range (1 GHz) near coincidences between the laser lines and the absorption gas signature.

Semiconductor lasers are continuously tunable over a broad spectral range. Our new apparatus uses PbSnSe diodes as the local oscillator and operates between 1050 and 1150 cm^{-1}.The effects of the characteristics of the diode on the performances of the heterodyne receiver have been studied. The power, the spectral width and the Relative Intensity Noise of the diode are important parameters.

High resolution heterodyne atmospheric spectra of the v_1 band of ozone have been recorded near 1120 cm^{-1}. The resolution (30 MHz $\approx 10^{-3}$ cm^{-1}) is lower than the Doppler width. With selected diodes, the spectral range is enhanced to 0.33 cm^{-1} (= 10 GHz) and permit to record entirely several lines.

The spectral range has been increased by a factor of 10 and high quality spectra have been recorded within 10 minutes

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**The NO dimer : Jet-cooled, low temperature spectra
of the v_1 and v_5 bands; matrix-isolation study
of the far-infrared bands.**

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The NO dimer has been observed with a FTIR spectrometer (Bruker IFS 120 HR) under thermodynamical equilibrium conditions using a low temperature White-type cell. Optical paths up to 44 meters allowed to record spectra of the v_1 and v_5 transitions at temperatures down to 130 K. In contrast to the spectra of the v_1 transition which exhibited a clear rotational structure, those of v_5 remained partly unresolved. This was attributed to the strong difference in the lifetimes of the v_1 and v_5 vibrational levels. Nevertheless, the rotational constants and an order of magnitude of these lifetimes could be extracted for both transitions. The equilibrium constant was also derived from spectra recorded at three different temperatures and this allowed us to obtain absolute line strength values. For the v_1 transition, some NO-broadened linewidths were also measured.

In order to corroborate the above results, additional spectra were taken in a molecular jet coupled to the FTIR spectrometer. The rotational cooling so-obtained allowed us to extract the lifetimes of the v_1 and v_5 vibrational levels under collision free conditions.

In view of a further theoretical calculation of the lifetimes, it was necessary to improve our knowledge of all vibrational frequencies of the dimer. A matrix isolation study of the very weak FIR transitions was then carried out. From the vibrational frequencies, an harmonic force field has then been derived.

Q4

COAXIALLY ORIENTED BEAM-RESONATOR ARRANGEMENT FOURIER TRANSFORM MICROWAVE (COBRA-FTMW) SPECTROSCOPY: LINE SHAPE AND LINE INTENSITY

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With the introduction of time domain microwave spectroscopy in a supersonic jet expansion application [1] in 1981, Flygare et al. also provided a description of the line shape obtained with the technique [2]. Even though they were able to treat the problem numerically and to derive analytical expressions for a number of special cases of the molecular beam expansion, an analytical treatment of the general experiment was not entirely feasible.

In the mean time a number of improvements and changes were introduced to the technique. Namely the coaxially oriented beam-resonator arrangement (COBRA) [3] [4] has dramatically improved the resolution and the sensitivity of the Fourier transform microwave (FTMW) spectrometer. Fortunately, the more favorable symmetry of the experiment in its current stage allows a complete analytical treatment. The presented expression will also include some extensions covering the radiation coupling and off-resonant excitation/detection.

[1] T. J. Balle and W. H. Flygare, Rev. Sci. Instrum. 52, 33(1981).
[2] E. J. Campbell, L. W. Buxton, T. J. Balle, M. R. Keenan, and W. H. Flygare, J. Chem. Phys. 74, 829(1981)
[3] J. U. Grabow and W. Stahl, Z. Naturforsch. 45a, 1043(1990).
[4] J. U. Grabow, W. Stahl, and H. Dreizler, Rev. Sci. Instrum. 67, 4072(1996).

HIGH-RESOLUTION ABSORPTION CROSS-SECTIONS OF NO₂ AT ATMOSPHERIC TEMPERATURES AND PRESSURES IN THE 12500 - 42000 CM⁻¹ RANGE

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Absolute absorption cross-sections of NO_2 at 293 K, 280K, 260 K, 246 K and 223 K in the wavenumber region between 12500 and 42000 cm^{-1} were measured using a Fourier-Transform Spectrometer BRUKER IFS 120 HR at resolutions of 0.5 cm^{-1} between 12500 cm^{-1} and 23000 cm^{-1} and of 1.0 cm^{-1} between 23000 cm^{-1} and 42000 cm^{-1}. At all temperatures, spectra at total pressures of 100 mbar and 1000 mbar were recorded.

The spectra were recorded using a double-jacketed coolable White-type absorption cell with a base length of 120 cm. For 4 different wavenumber regions, various combinations of detectors (Si diode, GaP diode, UV photodiode) and broad-band light sources ("super-quiet" Xe arc lamp, Quartz-Tungsten-Halogen lamp) were used. Measurements at 293 K, 280 K, 260 K and 246 K were performed under static conditions, whereas the 223 K measurements were carried out in a continuous flow of NO_2. A special gas-mixing system was used for filling the cell in the static measurements. Absolute NO_2 concentrations were determined from the NO_2 pressure in the gas mixing system when filling the cell in the static experiments. In the flow experiments, simultaneous measurements at room temperature in a short single-path reference cell were employed for this purpose. At all temperatures, the NO_2-N_2O_4 equilibrium was taken into account.

BrNO$_2$ (NITRYL BROMIDE) STUDIED BY HIGH-RESOLUTION FT-SPECTROSCOPY

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Laborory studies show that BrNO$_2$ is formed by heterogeneous reactions between HBr or NaBr and N$_2$O$_5$. Such reactions occur on polar stratospheric clouds and on sea-salt particles in the troposphere. Interestingly, there is little spectroscopic knowledge on the BrNO$_2$ molecule. BrNO$_2$ is chemically unstable and decomposes rapidly. Therefore, previous studies of BrNO$_2$ in the gas phase were only possible at low spectral resolution in flow experiments. In this work, BrNO$_2$ was synthesized by the reaction of highly diluted gaseous ClNO$_2$ with an aqueous Br$^-$ solution, and trapped at low temperature. The crude product was purified by trap-to-trap condensations and fractional sublimation *in vacuo*.

High-resolution infrared spectra of the ν_4 band of BrNO$_2$ around 1667 cm^{-1} were recorded with a spectral resolution of 0.0016 cm^{-1}, using a Bruker IFS-120 HR Fourier-Transform Spectrometer. Rotational constants for the ^{79}BrNO$_2$ and ^{81}BrNO$_2$ isotopomers have been determined for the $v_4 = 1$ and ground vibrational states. The spectral assigments and rotational constants show that BrNO$_2$ is a planar molecule of C_{2v} symmetry. Using infrared band centers of different isotopic species, the harmonic force field of BrNO$_2$ has been determined. The results are compared with a recent *ab-initio* study of the BrNO$_2$ molecule.

Near Infra-Red Tuneable Diode Laser Absorption Spectrometer using an Astigmatic Herriott Cell for the detection of the trace gases, CH_4 and N_2O

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Work has been carried out to develop a Tuneable Diode Laser Absorption Spectrometer(TDLAS) using Near Infra-Red Distributed Feedback(DFB) lasers to allow detection of the trace gas species, CH_4 and N_2O. Measurements will be taken at ground level and on a balloon platform. An Astigmatic Herriot Cell has been designed at Strathclyde University, providing a 100 m absorption pathlength in a 2 litre cell volume, giving the instrument high sensitivity and a fast response time. Second Harmonic Wavelength Modulation Spectroscopy (WMS) is used to provide sensitivity limits equivalent to a minimum detectable absorption of 10^{-7} in a 1 Hz bandwidth.
A programme of spectroscopic work to determine accurately the values for the absorption cross sections and broadening functions of all transitions likely to be used in the proposed atmospheric measurements is also being carried out.

Q8

STEREOCONTROL OF REACTIVE ENCOUNTERS USING POLARIZED LIGHT

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Abstract

Polarized light can be used to control the reaction geometry of selected species. One reactant A is generated in a photodissociation process. Its spatial distribution is completely described by the anisotropy parameter β. The other molecular reactant B is excited in a specific rovibrational state. Its spatial distribution is given by the j- and branch dependent alignment parameter $A_o^{(2)}$. We have studied the reaction of $X + HCN \rightarrow HX + CN$ with $X = H, Cl$. The attacking H atom is generated in the photodissociation of CH_3SH at 266 nm and the chlorine atom is formed in the photolysis of Cl_2 at 355 nm. In both cases the β-parameter is close to -1. In order to align the HCN partner reactant, the first and third vibrational overtone of the CH stretch vibration was excited via the R and P branches. The nascent $CN(v=0)$ product molecules were observed by laser induced fluorescence (LIF). The experimental results prove a preferred linear reaction geometry, i. e. an end-on attack of X atom on the terminating hydrogen atom of the HCN reactant.

Q9

FUNDAMENTAL AND FIRST HOT BANDS OF $O^{12}C^{17}O$ ISOTOPIC VARIANTS OF CARBON DIOXIDE

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Infrared spectra of a Carbon Dioxide sample enriched with Oxygen-17 have been recorded with a resolution of 0.0025 cm-1 in the regions of the three fundamental bands: v1 (1200-1400 cm-1), v2 (600-800 cm-1) and v3 (2200-2400 cm-1), using the long path difference Fourier Transform Spectrometer of the LPMA in Paris. The v_1 forbidden band of the slightly asymmetric species $^{17}O^{12}C^{18}O$, the v_3 fundamental bands and the $v_1 - v_2$, $2v_2 - v_2$ and $v_3 + v_2 - v_2$ hot bands of $^{17}O^{12}C^{17}O$ and $^{17}O^{12}C^{18}O$ have been studied for the first time. For each species a simultaneous reduction of all spectroscopic data has been carried out, yielding new or improved molecular constants. Line intensities of hot bands of $^{16}O^{12}C^{17}O$ have also been measured for the first time, and the corresponding rotationless transition moments and Herman-Wallis coefficients are reported.

ROTATIONAL RELAXATION IN THE CO_2-HE AND CO_2-AR MIXTURES : ENERGY CORRECTED SUDDEN APPROXIMATION MODELING FROM DOUBLE RESONANCE SPECTROSCOPY AND INFRARED ABSORPTION

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A time-resolved stimulated Raman-Infrared double resonance experiment[1] has been used to study collisional relaxation rates of energy levels in the CO_2-Ar and CO_2-He mixtures (10% CO_2, 90% rare gas).

In particular, we have studied the rotational relaxation of the (02^00) vibrational level. The total depopulation of the pumped rotational component $(14 \leq J \leq 34$; pressure < 3 Torr) and the rotational energy transfer signals $(\Delta J \leq 20$; pressure $= 10$ Torr) toward neighbouring levels have been observed. The time evolution of the rotational populations has been calculated through the modeling of the relaxation matrix by the energy corrected sudden approximation (ECS). The ECS parameters have been directly determined by fitting the experimental curves.

The same parameters had been determined previously from line-broadening data and line-mixing effects in infrared Q branches. They had been successfully tested in a number of IR bands including central regions at elevated pressure and the wing of $\Sigma-\Sigma$ bands.

The two sets of parameters determined from completely different experiments (double resonance and IR absorption) are in good agreement. This indicates the validity of the ECS approach for the modeling of both processes.

[1]   Cl. Roche et al., J. Chem. Phys. **101**, 2863 (1994)

Q11

MIXED ALGEBRAIC MODELS FOR LARGER LINEAR MOLECULES: U(2)⊗U(3)

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A mixed version of the vibron algebraic model has been developed to reproduce the vibrational energy pattern in larger linear molecules. The main object is to provide an alternative to conventional approaches. The general strategy consists in using U(2) algebras to describe the stretching vibrational part of the molecule and U(3) algebras for the (double-degenerate) bending part. Within such a scheme, explicit coupling terms in the algebraic Hamiltonian may be easily written down. The corresponding algebraic Hamiltonian is expressed through standard *Casimir, Majorana, Amat-Nilsen* and *off*-diagonal *Stretch-Bend* coupling operators of first and higher orders. The Hamiltonian matrix is then built in the local *anharmonic* vibrational basis. In order to achieve complete understanding of possible new features offered by the present model, we are carrying out preliminary tests on the acetylene molecule, C_2H_2. We will then extend our model to a larger molecule: *di*-acetylene, C_4H_2. This molecule has four stretching vibrational modes and four double-degenerate bending modes leading thus to an enforcement of the intramolecular dynamics. A more detailed discussion will be presented at the poster session.

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Phase Choices in the Matrix Elements of Angular Momenta, Directional Cosines and Symmetry Operators.

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It is demonstrated how the quantum mechanical solution to the problem of molecular rotation requires three and only three arbitrary choices of phases in the formulation of the matrix elements. These choices concern the phase factors f_s and f_m in the definition of the ladder operators for the angular momentum operators

$$\hat{J}_X + i\hat{J}_Y \,|\, J, k, m\rangle = |\, J, k, m+1\rangle f_s [(J-m)(J+m+1)]^{1/2}$$
$$\hat{J}_y + i\hat{J}_x \,|\, J, k, m\rangle = |\, J, k+1, m\rangle f_m [(J-k)(J+k+1)]^{1/2}$$

and a third phase factor, f_J, appearing in matrix elements of the directional cosines off diagonal in J, e.g.

$$\langle J-1, k, m |\, \hat{\Phi}_{Zz} \,|\, J, k, m\rangle = 2 f_J \left[\frac{(J^2 - k^2)(J^2 - m^2)}{J^2(2J-1)(2J+1)} \right]^{1/2}$$

The important fact is that f_s and f_m have an impact on the matrix elements of the directional cosines off diagonal in m or k respectively, e.g.

$$\langle J-1, k, m |\, \hat{\Phi}_{Zy} \,|\, J, k-1, m\rangle = f_m f_J \left[\frac{(J-k)(J-k+1)(J^2 - m^2)}{J^2(2J-1)(2J+1)} \right]^{1/2}$$

If this is not properly taken care of, errors may be introduced when higher order effects in intensity calculations are taken into account. Furthermore the matrix elements of the symmetry operators are affected. More examples of explicit formulas involving the phase factors are presented.

Q13

ROTATIONAL SPECTRA OF PHOSPHORUS MONOSULFIDE UP TO 1 THz

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The Cologne terahertz spectrometer has been used to measure the rotational spectra of phosphorus containing molecules. Terahertz spectra of PS are presented here.

The PS radical in its $^2\Pi$ electronic ground state has been produced by discharging $PSCl_3$ buffered with Ar. The lower rotational transitions of PS, corresponding to its relatively high mass, fall into the 40 GHz region and are yet observed up to 300 GHz[1]. We continued these series up into the terahertz region as high as J values near 50.5. For all transitions the Λ-doubling was resolved for both the $^2\Pi_{\frac{1}{2}}$ and the $^2\Pi_{\frac{3}{2}}$ electronic ground states. The Λ-doublett parameters could be determined, including their centrifugal distortion correction terms p_D and q_D. The hyperfine structure (hfs) caused by the P-atom could be partially resolved. The sensitivity of the spectrometer allowed measurements of weak hfs components corresponding to very small intensities of about 0.001 %. Owing to these hfs transitions all parameters of the magnetic hfs as well as the second order interaction C_I of the nuclear spin rotation constant of the molecule have been determined for the first time.

In future, the light radical PH will be investigated. Both PS and PH are of astrophysical interest, since identifications of phosphorus containing molecules in the interstellar medium turned out to be very rare up to the present.

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[1] Ohishi et al. 1988

Q14

CALCULATED PHOTOELECTRON SPECTRA OF CCl_2F AND H_2NO

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The vibrational structure of the photoelectron (PE) spectra of CCl_2F and H_2NO has been calculated ab initio, making use of anharmonic vibrational wave functions from variational calculations. The calculated PE spectra have a rather complex vibrational structure caused by a substantial changes of the equilibrium bond lengths and angles. There are pyramidal-planar (CCl_2F) and (quasi-)planar-planar (H_2NO) transitions.

The PE spectrum of CCl_2F shows several long progressions of the out-of-plane vibration υ_4 in combination with the symmetric CCl_2 stretching vibration υ_2 and the CF stretching vibration υ_1 ($a*\upsilon_1+b*\upsilon_2+n*\upsilon_4$; a,b=0,1,2,3). Some comparison is possible with the results of REMPI spectroscopy.[1]

The adiabatic transition dominates the first three bands ($\tilde{X}$ $^1A_1$, $\tilde{a}$ $^3A''$ and $\tilde{A}$ $^3A_2$) of the PE spectrum of H_2NO which are observed by PE spectroscopy.[2] The fourth band ($\tilde{b}$ $^3A_1$) shows a long progression of the NO stretching vibration.

[1] B. P. Tsai, R. D. Johnson, III and J. W. Hudgens, J. Phys. Chem., 93, 5334 (1989).

[2] J. Baker, V. Butcher, J. M. Dyke and A. Morris, J. Chem. Soc. Faraday Trans. II, 86, 3843 (1990).

THE 3d FORMALISM
AND SOME OF ITS APPLICATIONS

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A particular algebraic treatment, called 3d formalism and related to a three oscillator system, is proposed and described in detail in Ref.[1]. Here, we summarize the building scheme used and the main results: arbitrary 3d tensor operators, which can be expressed in terms of elementary boson operators, are built through the chain $U(3) \supset SO(3) \supset SO(2)$; their matrix elements are obtained from the Wigner Eckart theorem applied at the $SO(3)$ level.

The 3d formalism mentioned above is a quite general mathematical tool which may be applied (or exploited) in different ways. Here, we investigate the existing connections with other formalisms used in molecular spectroscopy, such as:

- the Hecht's formalism associated with a three fold degenerate vibrational mode in spherical tops,

- the rovibrational vibron model $U(4)$ introduced by Iachello et al. for diatomic molecules.

Also, a recent theoretical extension we made, in order to extend the $U(4) \times U(4)$ dynamical approach to the rovibrational spectroscopy of triatomic molecules, will be presented. We hope that this should lead to new interesting resonance terms in the vibron model Hamiltonian of such molecules.

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[1] V. Boujut and F. Michelot, accepted to J. Mol. Spectrosc.; V. Boujut, *thesis*, Dijon (France), 1996.

LASER SPECTROSCOPY OF THE Ã $^2\Pi \leftarrow \widetilde{X}\,^2\Sigma^+$ TRANSITION OF YTTERBIUM MONOACETYLIDE

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The first spectroscopic identification and characterization of ytterbium monoacetylide (YbCCH) is reported. By combining resonance enhanced two photon ionization (R2PI), laser induced fluorescence (LIF), and photoionization efficiency spectroscopy (PIE) with density functional calculations the $\widetilde{X}\,^2\Sigma^+$ and the Ã $^2\Pi_{1/2,3/2}$ states of YbCCH as well as the $\widetilde{X}$ $^1\Sigma^+$ state of YbCCH$^+$ have been characterized. The Ã $^2\Pi_{1/2,3/2}$ - $\widetilde{X}$ $^2\Sigma^+$ system whose 0-0 band for the Ã $^2\Pi_{1/2}$ component lies at around 16848 cm^{-1} for YbCCH has been studied at 0.3 cm^{-1} resolution. The excitation spectra, both R2PI and LIF are characterized by progressions involving the YbCC bending mode (v_5) whose wavenumber has been determined to be 96 cm^{-1} and 103 cm^{-1} for the $\widetilde{X}^2\Sigma^+$ and Ã $^2\Pi_{1/2,3/2}$ state, respectively. The dispersed fluorescence spectra show a progression in the Yb-C stretching vibration with a wavenumber of $\omega(v_3)$ = 328 cm^{-1} . Density functional calculations confirmed the vibrational assignment and yielded a linear geometry for both the $\widetilde{X}$ and Ã state of YbCCH as well as for the $\widetilde{X}$ $^1\Sigma^+$ state of the cation state. Photoionization efficiency spectroscopy yielded an adiabatic ionization potential of 47165(10) cm^{-1} (5.8477(12) eV). Rydberg series converging to the 5_1 and 5_2 level of YbCCH$^+$ were observed and combined with the appearance potentials led to $\omega(v_5)$ = 97 cm^{-1} for the YbCC bending mode of YbCCH$^+$. High resolution spectra of several isotopomers have been analyzed and the results will be presented.

THE c $^3\Sigma^+$ - b $^3\Pi_r$ AND g $^3\Sigma^+$ - b $^3\Pi_r$ TRANSITIONS
OF THE SIO MOLECULE

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The c $^3\Sigma^+$ - b $^3\Pi_r$ transition of SiO has been observed in emission in a microwave discharge through Helium with traces of $SiCl_4$ and O_2 with a Bruker IFS 120 at high resolution. The rotational analysis yields more precise molecular constants for the two states involved than the previous study of Nagaraj and Verma (1970). Using the new constants for the b $^3\Pi_r$ state, better constants are also obtained for the g $^3\Sigma^+$ (4sσ) state analysed by Singh et al. (1974).

Q18

Submillimeter Wave Absorption Spectroscopy of the Ar–CO van der Waals Stretching Vibration

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The ν_3 van der Waals stretching vibration of Ar–CO complex was investigated in the submillimeter wave range by a new backward wave oscillator (BWO) – pulsed supersonic jet spectrometer at Cologne.

The radiation with typically 10 mW power generated by a phased stabilized BWO was focused by a teflon lens into a vacuum chamber with a jet and collected by a second lens onto a liquid helium cooled InSb bolometer. A double modulation scheme employing a 15 kHz wavelength modulation of the BWO and an 80 Hz jet modulation was used for the detection of the absorption signal in the jet. The minimum detectable fractional absorption 2×10^{-7} was evaluated for the present setup by measuring the $J = 5 \leftarrow 4$ rotational transition of $C^{18}O$.

Altogether 13 rovibrational transitions belonging to R and P branches of the $K_a = 0 \leftarrow 0$, $v_3 = 1 \leftarrow 0$ parallel band of Ar–CO were detected for the first time between 530 and 600 GHz. The quantitative spectroscopical analysis is complicated by the strong Coriolis interaction between the upper $K_a = 0, v_3 = 1$ state and the $K_a = 1$, $v_2 = 1$ state of the excited bending vibration. The results of the analysis will be presented.

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Tunneling Splitting Patterns in the K = 0 and 1 Levels of $(CH_3OH)_2$

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Based on an IAM-like group-theoretical formalism previously developed and an analysis made for the $K=0$ a-type microwave transitions using this formalism, microwave transitions involving $K = 1$ as well as $K = 0$ levels, which have been measured extensively by using the Fourier transform nozzle jet spectrometer at NIST, were analysed to obtain detailed information on the tunneling splitting patterns in the $K = 0$ and 1 levels. In addition to the transition-frequency and line-assignment data for the a- and b-type transitions given by Lovas and Hartwig (1), several c-type transitions as well as a- and b-type transitions were newly observed and assigned in the course of present study. All the assigned transitions were treated on the basis of the present formalism, and the main aspects of tunneling splitting patterns in the $K = 0$ and 1 states were determined. For example, the apparently strange behavior in degenerate E and G species of tunneling splittings due to lone-pair exchange motion on the acceptor methanol, and also of the transition selection rules, was interpreted reasonably on the basis of the present formalism. As a result of the present study, the magnitude of the tunneling splitting due to the lone-pair exchange motion was determined.

(1) F. J. Lovas and H. Hartwig, J. Mol. Spectrosc. to be published.

Q20

MB-FTMW SPECTRA OF THE HYDROGEN BONDED DIMERS
FURAN···HF, 2,5-DIHYDROFURAN···HF, TETRAHYDROFURAN···HF
AND TETRAHYDROFURAN···HCl

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The rotational spectra of the hydrogen bonded dimers furan···HF,
2,5-dihydrofuran···HF (DHF···HF), tetrahydrofuran···HF (THF···HF) and
tetrahydrofuran···HCl (THF···HCl), have been measured in the frequency
range from 6 to 18.5 GHz using a molecular beam Fourier transform
microwave spectrometer. The rotational and quartic centrifugal distortion
constants, the D_{aa} H,F nuclear spin-nuclear spin coupling contants for the HF
complexes and the Cl-nuclear quadrupole coupling constants for the different
isotomomers of the HCl dimer have been determined.

These constants have been interpreted in terms of the formation of a
hydrogen bond by the hydrogen halides with the oxigen atom of the ring
molecules with piramidal arrangements for DHF···HF, THF···HF and
THF···HCl and C_{2v} symmetry for furan···HF with the HF subunit lying on
the C_2 axis.

A doubling of the spectra has been observed for DHF···HF,
THF···HF and THF···HCl. The vibration-rotation coupling observed
between the components of the splitting for the THF complexes indicate that
the doubling is due presumably to pseudorotation. The doubling for
DHF···HF may be attributed to the interconversion between the two
equivalent piramidal arrangements of HF at the O atom of DHF.

Effective Rotational Hamiltonian for Dimethyl Ether: Microwave and mm-wave Spectra of Ground and Two Torsional Excited States

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An effective rotational Hamiltonian for molecules with two periodic large-amplitude motions[1] was used to analyze the rotational spectrum of dimethylether, CH_3OCH_3. For the analysis of the vibrational ground state, (00), microwave[2,3] and mm-wave[4] data from the literature were combined with new measurements between 100 and 550 GHz in a global fit of all four torsional substates. Frequencies between 8 and 550 GHz were fit for transitions involving energy levels with J up to 40 and K_a up to 9. Only 22 spectroscopic parameters were necessary to fit 1561 frequencies to experimental precision (dimensionless standard deviation 0.53). The following parameters were determined in the least-squares fit: $\rho = 0.21648(20)$, $\beta = 8.509(25)°$, parameters equivalent to the rotational, quartic and sextic distortion constants, the internal energy tunneling parameters $\varepsilon_{01} = -3.0451(39)$ MHz and $\varepsilon_{02} = 0.0033(15)$ MHz and three tunneling constants related to the "rotational" constants.

The microwave data of the two lowest torsional excited states[2,5] were combined with new measurements between 262 and 344 GHz made with the fast scan submillimeter spectroscopic technique (FASSST). For the excited state of the infrared inactive torsional mode, (10), only 27 parameters were necessary to fit over 350 frequencies ($J \le 40$, $K_a \le 7$) of all torsional substates to a dimensionless standard deviation of about 2.1. For the excited state of the infrared active torsional mode, (01), a comparable fit was only possible for transitions involving energy levels with $J \le 40$ and $K_a \le 5$ although transitions involving energy levels with $K_a = 6$ were identified. The internal energy tunneling parameters are about 27 times larger than for the ground state.

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Q22

Millimeter-Wave Spectroscopy and Structure of
Chloroform

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The Ground vibrational states of the two main isotopic species of chloroform ($H^{12}C^{35}Cl_3$ and $H^{12}C^{37}Cl_3$) have been the subject of several investigations in the millimeter wave region (1-2). But as far as we know, no study has been reported on the asymmetric isotopomers.

We present here new results obtained for all the 12 possible ^{12}C-, ^{13}C-, and D-substituted forms. Measurements were carried out in selected ranges from 145 to 470 GHz, which corresponds J values between 22 and 70.

Accurate molecular parameters, up to sextic terms are determined.

Different experimental structures (r_o, r_s, r_z, r_m^ρ) are determined and compared to *ab initio* structures calculated at different levels of theory.

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STRUCTURAL AND CONFORMATIONAL PROPERTIES OF 1,2-DIFLUOROPROPANE AS STUDIED BY MICROWAVE SPECTROSCOPY AND QUANTUM CHEMICAL COMPUTATIONS[1]

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The MW spectrum of 1,2-difluoropropane has been investigated in the 10.0 - 40.0 GHz spectral region at dry-ice temperature. 3 all-staggered conformers are possible for this compound. Two of these rotamers denoted **Conformer I** and **II**, respectively, were assigned in this work. These two forms both have a F-C-C-F *gauche* atomic arrangement. The methyl group is *anti* to the C1-F bond in **Conformer I** and *gauche* to this bond in **Conformer II**. The third form, **Conformer III**, which has a F-C-C-F *anti* arrangemet, is likely to be present but could not be assigned, presumably because of its small dipole moment. **Conformer II** is 1.2(4) kJ mol^{-1} more stable than **I**. The dipole moments (in units of 10^{-30} C m) are $\mu_a = 5.12(4)$, $\mu_b = 8.64(8)$, $\mu_c = 0.11(2)$, and $\mu_{tot.} = 10.05(8)$ for **Conformer I**, and $\mu_a = 1.108(3)$, $\mu_b = 4.46(3)$, $\mu_c = 8.30(6)$, and $\mu_{tot.} = 9.49(6)$ for **Conformer II**, respectively. Three vibrationally excited states of **I** belonging to three different normal modes, were assigned while two such excited states were assigned for **II**. The barrier to internal rotation of the methyl group in **Conformer I** was determined from the splittings of the first excited states of the methyl group torsional vibration and is 11.88(20) kJ mol^{-1}. The microwave work has been assisted by *ab initio* computations at the MP2/6-311++G** (frozen core) level of theory, as well as density theory calculations at the B3LYP/6-311++G** level.

Vibration-rotation spectroscopy of the C_2D radical by CO-overtone Faraday-laser magnetic resonance

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We present rotationally resolved spectra of the 2 (3513 cm^{-1})   X2 (0,1,0) vibronic transition of the C_2D radical. Using a Faraday-laser magnetic resonance spectrometer in combination with a CO-overtone laser we could observe gas phase transitions originating from the X2 (0,1,0) vibronic state for the first time.

The C_2D radicals were generated by a dc-excited discharge in a gas mixture of acetylene C_2H_2 and deuterium D_2 in helium. Some modifications to the design of the discharge cell allowed extensive measurements under stabel generation conditions of the C_2D radical.

The first excited electronic state A2 (0,0,0) of the C_2D radical lies near the electronic ground state in the 3500 cm^{-1} region. So there is a strong mixing of the A2 (0,0,0) state with the vibronic X2 (0,1,2) and X2 (0,7,1) states. The effective orbital g-factor of the upper A2 (0,0,0) state was derived from the experiment. Together with the latest *ab initio* calculations on the C_2D radical this gives information of the mixing ratios of the upper state and the distance of the electronic - and - energy potential surfaces.

Based on the final analysis of the spectroscopic data we are now able to give the gase phase term value of the X2 (0,1,0) vibronic state with an accuracy of 0.001 cm^{-1}.

Q25

STUDY OF CARBONYL SULPHIDE (INCLUDING RARE
ISOTOPOMERS) BY MM-WAVE, CO_2 SIDEBAND,
STARK , AND LMDR SPECTROSCOPIES .

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The millimeter-wave spectrum has been investigated from 154 to 160
GHz and from 231 to 240 GHz using enriched products, with particular
interest to highly excited states. The following isotopomers have been
observed : $^{16}O^{12}C^{32}S$, $^{16}O^{12}C^{34}S$, $^{16}O^{13}C^{32}S$, $^{16}O^{12}C^{33}S$, $^{16}O^{13}C^{34}S$, $^{17}O^{12}C^{32}S$,
$^{16}O^{12}C^{36}S$, $^{18}O^{12}C^{34}S$, $^{16}O^{13}C^{33}S$, $^{18}O^{13}C^{32}S$, $^{18}O^{12}C^{33}S$, $^{17}O^{13}C^{32}S$, $^{16}O^{13}C^{36}S$,
$^{18}O^{13}C^{34}S$, $^{18}O^{13}C^{33}S$, and $^{18}O^{13}C^{36}S$.

The CO_2 laser sideband spectra of natural OCS concern 7 lines of the
02^00-00^00 band and 13 lines of the 03^10-01^10 band of $^{16}O^{12}C^{32}S$. The
resolution is in the range of 300 kHz and the absolute accuracy is 20 kHz
(better than 10^{-6} cm^{-1}).

Complementary CO laser saturation Stark measurements have been
performed in the 00^01-00^00 and 12^00-00^00 bands, and their associated hot
bands. The following isotopomers have been observed : $^{16}O^{12}C^{32}S$, $^{16}O^{12}C^{34}S$,
$^{16}O^{13}C^{32}S$, $^{18}O^{12}C^{32}S$, $^{16}O^{13}C^{34}S$, $^{18}O^{12}C^{34}S$, $^{18}O^{13}C^{32}S$, $^{17}O^{13}C^{32}S$, $^{18}O^{13}C^{34}S$,
and $^{18}O^{13}C^{33}S$.

Intracavity Laser-Microwave Double Resonance measurements in
presence of Stark field have been performed with a CO laser. They concern the
ν_3 band of $^{16}O^{13}C^{32}S$ and its first hot band.

300

Q26

SYMMETRIC AMINO-WAGGING BAND OF HYDRAZINE

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The inversion motions of two equivalent amino group of hydrazine, N2H4, give rise of two infrared fundamental bands: the symmetric, v_6, and antisymmetric, v_{12}, wagging. In a low resolution spectrum the symmetric band appears as a small hump in a P branch of the antisymmetric band. When from a newly recorded high-resolution infrared spectrum of hydrazine in the 729-1198 cm^{-1} region then lines of the strong symmetric band had been removed most of the remaining lines between 729 and 900 cm^{-1} could be assigned as PP, PR, RR, RP, RQ and PQ series of the symmetric band. About 1500 transitions up to K' = 7 have been assigned. This is the first analysis of the rotationally resolved symmetric wagging band. The band center is located at 792 cm^{-1} which is higher then the value given from earlier analyses of low resolution infrared spectra. The structure of inversion splittings is discussed.

Infrared Laser Spectroscopy of Phosphorus Analogues of N_2O

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While the infrared spectroscopy of nitrogen oxides has been extensively and accurately studied it is only very recently that analogous species containing phosphorus have been detected. The oxidation of phosphorus proceeds via a complex chain reaction which is surprisingly different from nitrogen oxidation and which opens the door to a range of novel phosphorus oxide species.

In this work we describe the detection of P_2O using an infrared diode laser system and multi-pass cell. The P_2O is produced directly in the cell using carefully controlled discharge flow techniques. Over 40 transitions in the v_3 stretching fundamental (the P=O stretch) have been observed near 1277.6 cm^{-1} and analysed to produce an accurate set of molecular constants and to confirm the structure as linear and non-symmetric PPO. The lowest bending level is calculated to occur about 200 cm^{-1} above the ground state and so not surprisingly hot-band transitions originating from this level are observed. The $(01^10) \leftarrow (01^10)$ band has an origin near 1274.9 and the transitions show characteristic l-type doubling. The molecular constants determined for P_2O are remarkably similar to those predicted by scaling known constants of N_2O and agree well with theoretical predictions.

To access the possibility of observing other triatomic oxides, and in particular the mixed phosphorus/nitrogen species, *ab initio* calculations using the density functional approach have been carried out for the expected isomers. Good agreement with the experimental values of the vibrational and rotational constants is obtained for P_2O and N_2O. Unlike N_2O, P_2O is predicted to have a low lying cyclic isomer which may be experimentally accessible. The *ab initio* calculations predict the PNO isomer to be the most stable mixed form, with the N=O stretching vibration near 1800 cm^{-1} being particularly intense. This prediction supports the assignment of a transition at 1755 cm^{-1} observed in matrix studies to PNO and thus this species must be a good candidate for gas phase detection. In experiments currently in progress we have detected, using mixed P/N/O chemistry, a large number of lines corresponding to a transient linear molecule with a 2B spacing in reasonable agreement with *ab initio* values.

Q28

The High-Resolution IR Spectra of the ν_{14}, ν_{17} and ν_{18} Bands of Diborane

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We are in the process of recording and analyzing all of the IR active fundamental bands of B_2H_6, the simplest of the hydrogen bridged borane compounds, with the goal of determining the frequencies of the IR forbidden modes in this very symmetric (D_{2h}) molecule by means of anharmonic interactions. The spectra were obtained on a Bruker 120HR FT spectrometer with a spectral resolution of 0.002 cm^{-1}. The sample contained boron in natural abundance (~19% ^{10}B, ~81% ^{11}B), and, therefore, the abundances of $^{11}B_2H_6$, $^{10}B^{11}BH_6$, and $^{10}B_2H_6$ were 66% ,31% and 4% respectively. With the resolution available, the spectra of the two most abundant species were readily assignable. At this point, the ν_{14}, ν_{17} and ν_{18} bands have been recorded and assigned. Greatly improved ground state constants have been obtained, and a mixed r_s-r_0 structure for the molecule has been obtained. All bands suffer perturbations, and their energy levels have been fit with a model taking into account the necessary Fermi or Coriolis interactions. The most significant finding at this point is the determination of the ν_9 vibrational frequency (937.27(44) cm^{-1} in $^{11}B_2H_6$, 940.15(31) cm^{-1} in $^{10}B^{11}BH_6$). Although this band is IR active, it has never been observed directly.

Q29

THE ICLAS OVERTONE SPECTRUM OF H_2S ABOVE 12200 cm^{-1}

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Some selected rovibrational bands of the overtone spectrum of H_2S have
been studied by the intracavity laser absorption spectroscopy (ICLAS) in the
wavenumber region 12200 - 15500 cm^{-1}. The resolution of the spectrometer
is about 0.02 cm^{-1}. The studied band systems are labelled as $41^{\pm}0$, $50^{\pm}1$,
$60^{\pm}0$, and $60^{\pm}1$ in the local mode notation. In addition to the H_{22} type
interaction coupling the bands of the local mode pair, the band systems show
several global and local perturbations. These perturbations and the states
involved have been analysed explicitly by a Watson-type Hamiltonian with
appropriate off-diagonal Fermi and α resonance operators. A local mode
type behaviour is clearly evidenced by the values of the rotational
parameters. Also the theoretically predicted formation of four-member
groups of rovibrational levels at high rotational excitations is confirmed.

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Q30

FOURIER TRANSFORM SPECTRUM OF THE H_2S MOLECULE IN
5600 - 6800 CM^{-1} (SECOND HEXAD) REGION

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The second hexad ((031), (130), (111), (210), (012), (050)) of the H2S resonating states was analyzed using spectra recorded at 0.011 cm^{-1} resolution with the Kitt Peak Fourier transform spectrometer . About 900 precise experimental energy levels were derived after the spectrum assignment for $H_2^{32}S$, $H_2^{33}S$, and $H_2^{34}S$ species that two times exceeds the data of Ref.[1] The assignment process has been followed by the rotational constants refinement. It has been shown that, begining with J=10, large resonance perturbations appear between (111), (210), (031) and (130) states wich were not taken into account in Ref.[1]

Transformed transition moment expansion parameters have been retrieved from the fitting to more than 1000 main isotope experimental line intensities. Precise synthetic H_2S absorption spectrum has been finally generated in an analyzed region.

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Q31

THE JET COOLED FTIR SPECTRUM OF ETHANE

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We have recorded the high resolution jet cooled spectrum of ethane between 1200 and 6000 cm^{-1} using a Bruker IFS120HR Fourier Transform interferometer and a large slit jet apparatus [1]. The resolution was varied from 0.005 to 0.04 cm^{-1}. Numerous bands were observed, several of them not reported or analyzed in detail before. We shall show examples of the recorded spectra which demonstrate the impressive simplification due to the rotational cooling, in particular regarding the removal of torsional hot bands. We shall further present an analysis concerned with a system of combination bands located between 4000 and 4500 cm^{-1}. Several perpendicular bands in this region could be assigned on the basis of the observed Coriolis ζ constant. Effective rotational parameters were determined for these bands analyzing individual subbands separately.

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HIGH RESOLUTION ANALYSIS OF THE COMPLEX SYMMETRIC CF$_3$ STRETCHING CHROMOPHORE ABSORPTION IN CF$_3$I

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The present investigation completes a series of previous high resolution studies on the symmetric CF-stretching fundamental (ν_1) of CF$_3$I [1-3]. New pulsed slit jet diode laser spectra (instrumental bandwidth $\approx$ 0.0008 cm^{-1}) of CF$_3$I (neat or seeded in He) at rotational temperatures of about 7, 30 and 70 K have been obtained in regions 1068.55-1071.0, 1073.6-1075.25, 1077.75-1078.9 and 1081.4-1082.6 cm^{-1}. The low J, K part of the available transitions could be perfectly fitted by a model including the anharmonically coupled levels ν_1, $2\nu_5^0$ and $\nu_3 + 3\nu_6^{\pm 3}$, and the local Coriolis perturber $\nu_3 + 3\nu_6^{+1}$. The level $\nu_3 + 3\nu_6^{+3}$ was observed and included for the first time, and an additional anharmonic coupling between the levels $\nu_3 + 3\nu_6^{+3}$ and $\nu_3 + 3\nu_6^{-3}$ proved to be relevant. In order to analyse the higher J, K regions, perturbations arising from $2\nu_5^{\pm 2}$ turned out to be important. In distinct regions of the spectra, effects due to nuclear quadrupole interaction are clearly visible. The results are discussed in relation to ultrahigh resolution studies of IR- multiphoton excitation of CF$_3$I [4,5].

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Q33

ON THE MODELING OF IR ABSORPTION IN THE FAR BAND WINGS OF CO_2 PERTURBED BY RARE GASES

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The understanding of the nature of absorption in the far wings of CO_2 vibrational bands can shed a new light on the general mechanisms of continuous absorption in the atmospheric windows.

It is widely held belief that departures from the Lorentzian line-shape are mainly due to the line-mixing effect and finite duration of collisions. The data of recent experiments (see Ref.[1]) carried out in the far wings of v_3 and $3v_3$ absorption bands of CO_2 perturbed by He and Ar at very high densities (up to 1000 bar) have been considered in Ref.[1] in terms of quasistatic binary approximation in account for the finite duration of collisions. Present work shows that these experimental data can be interpreted in a different way, taking into account the formation of Van der Waals CO_2-$(Rg)_n$ complexes. Linear density term in the far wing absorption can be ascribed to formation of 1:1 intermolecular complex. The nonlinear density effect, discussed in Ref.[1] in terms of the finite volume of interacting molecules, is due to ability of CO_2 molecule to form complexes with higher rare gas polymers.

More general problem is addressed, how to discriminate between various spectroscopic manifestations of intermolecular interactions. Present work emphasizes the need to perform thorough statistical physics partitioning of tightly bound, metastable and free intermolecular states in the phase space.

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Sextic Centrifugal Distortion Parameters for Near Local Mode Molecules

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Earlier derived Ref.(1) "expanded local mode method" was used for the analysis of sextic centrifugal distortion parameters for XY_2 (C_2v), XY_3 (C_3v), and XY_4 (T_d) type molecules, which satisfy the conditions of the expanded local mode approach. Simple relations, both between sextic centrifugal parameters themselves, and between sextic and quartic ones of the above molecules were obtained. General theoretical results are compared with the experimental values of corresponding parameters for the H_2S, H_2Se, AsH_3 molecules.

1. O.N. Ulenikov, R.N. Tolchenov, and Qing-Shi Zhu, Spectrochimica Acta, Part A, **52**, 1829-1841 (1996).

R1

HIGH RESOLUTION OPTICAL SPECTROSCOPY
IN MOLECULAR BEAMS[*]

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Following a brief introduction to the technique, this talk will describe several recent applications of high resolution optical spectroscopy in molecular beams. Of particular interest are studies of the hydrogen bonded complexes of water and ammonia with UV-absorbing chromophores including 2-pyridone, indole, and 1- and 2-naphthol The results provide new insights into both the structures of the different complexes and their dynamical behaviour following the absorption of light, along both reactive and non-reactive pathways. Especially interesting to us are the possible roles of the Solvent in promoting such processes.
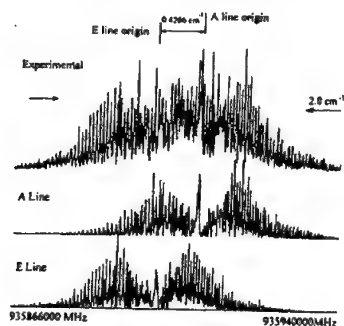
FIG. 1. The rotationally resolved fluorescence excitation spectrum, of the $S_1 \leftarrow S_0$ electronic origin of trans-1 -hydroxynapthalene-NH$_3$.
S. J. Humphrey and D. W. Pratt, J. Chem Phys. **104**, 8332 (1996)

APPLICATIONS OF HIGH RYDBERG SPECTROSCOPY IN
CHEMICAL DYNAMICS

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The spectroscopic study of molecular Rydberg states may be viewed as an opportunity to probe the scattering of an electron from a molecular ion core. A high-n Rydberg state may be characterised by a set of core quantum numbers $[v^+, J^+.....]$ and a set of atomic-like Rydberg electron quantum numbers $[n, l, s, j]$. The details of interactions between the various Rydberg series (or 'channels') characterised by different values of the Rydberg angular momentum or ion core quantum numbers provide information on the molecular ion charge distribution. For example, in nitric oxide the quadrupole and to a lesser extent the small dipole of the ion core can induce such couplings.

In this paper we present new results involving experimental measurements of the Stark effect in autoionizing Rydberg states of NO, using two colour laser excitation. The effect of the applied external field on the Rydberg electron competes with the internal field due to the ion-core, and as the field increases internal couplings may be switched off. The Stark spectra, although more complex than the zero field spectra, are much more revealing with regard to the nature of the interactions induced by the internal field. The extension of MQDT to interpret the results of these Stark measurements is a challenging computational problem and some preliminary calculations are presented here. Whereas the zero-field spectra only involve the interaction of 5-10 channels, the Stark spectra require incorporation of several hundred channels, including all possible l values.

External fields not only perturb the spectral line positions and intensities, but also have profound effects on lifetimes of metastable Rydberg states, a feature which underlies the success of pulsed-field ionization (PFI) techniques such as ZEKE spectroscopy. The Stark spectra of NO presented here, provide new information on the nature of such lifetime perturbations.

We also report on the measurement of a series of rotationally resolved pulsed-field ionization spectra of the ammonia molecule, obtained by 2+1' two-colour excitation via the B' and C intermediate Rydberg states. The possibility for producing ammonia ions in selected v^+, J^+ and K^+ is demonstrated with a view to studying ion-molecule reactions involving these state-selected species. The PFI spectra reveal a wealth of Rydberg channel interactions, allowing a rare insight into the nature of such couplings in polyatomic species. The full interpretation of PFI spectra requires a detailed characterisation of such channel interactions and we demonstrate the potential of MQDT as a means for understanding the spectra.

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